Investigations of fiber optic temperature sensors based on Yb:Y3Al5O12

Jermaine L. Kennedy
University of South Florida

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Investigations of Fiber Optic Temperature Sensors Based on Yb:Y$_3$Al$_5$O$_{12}$

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of
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<tr>
<td>A</td>
<td>Amps</td>
</tr>
<tr>
<td>CJC</td>
<td>Cold Junction Condensation</td>
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<tr>
<td>CW</td>
<td>Continuous Wave</td>
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<tr>
<td>Er</td>
<td>Erbium</td>
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<tr>
<td>FDR</td>
<td>Fluorescence Decay Rate</td>
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<td>FWHM</td>
<td>Full Width at Half Maximum</td>
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<tr>
<td>IGCC</td>
<td>Integrated Gasification Combined Cycle</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<tr>
<td>LHPG</td>
<td>Laser Heated Pedestal Growth</td>
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<tr>
<td>mm</td>
<td>Millimeter</td>
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<tr>
<td>mW</td>
<td>Milliwatt</td>
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<tr>
<td>Nd</td>
<td>Neodymium</td>
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<tr>
<td>NIR</td>
<td>Near Infrared</td>
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<tr>
<td>nm</td>
<td>Nanometer</td>
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<tr>
<td>RF</td>
<td>Radio Frequency</td>
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<tr>
<td>RTD</td>
<td>Resistance Temperature Detectors</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>μm</td>
<td>Micrometer</td>
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<tr>
<td>YAG</td>
<td>Yttrium Aluminum Garnet</td>
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<tr>
<td>YbAG</td>
<td>Ytterbium Aluminum Garnet</td>
</tr>
<tr>
<td>Symbol</td>
<td>Element</td>
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<tr>
<td>--------</td>
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</tr>
<tr>
<td>Yb</td>
<td>Ytterbium</td>
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<tr>
<td>Y</td>
<td>Yttrium</td>
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Investigations of Fiber Optic Temperature Sensors Based on Yb:Y₃Al₅O₁₂

Jermaine L. Kennedy

ABSTRACT

This dissertation presents the development of temperature sensors which employ a fiber-optic probe consisting of single crystal Y₃Al₅O₁₂ (YAG) fiber with a phosphor of short length grown directly onto one end using the laser heated pedestal growth method. The response of all the crystalline temperature sensors derives from the temperature-dependent decay time of fluorescence. Yb³⁺ ions served as the fluorescer, while the addition of various rare-earth codopants (i.e., Nd³⁺ and Er³⁺) with Yb³⁺ provided an additional path in the form of phonon assisted energy transfer. With the additional nonradiative decay path, the temperature sensors exhibited a more desirable response.

A thermally compensated fluorescence decay rate fiber optic temperature sensor was demonstrated for the first time experimentally to the best of our knowledge to make accurate surface temperature measurements. Overall, this novel technique is envisioned to aid in the perpetual challenge of precise surface temperature measurements in comparison to current methods, with the emphasis in the area of rapid thermal processing of semiconductors.
CHAPTER 1

INTRODUCTION

1.1 Background Information on the Proposed Research

As one of the seven basic quantities in the SI (International System of Units) system, temperature is probably the most measured physical parameter since virtually every process in nature and industry is temperature dependent. The accelerating proliferation of technology in the applied fields of science, engineering and medicine has led to an ever-increasing variety of situations that requires the knowledge of the accurate temperature of some system, process, component or specimen. As a result, new techniques and instrumentation are needed depending on temperature measurement requirements in different processes and working environments.

One novel instrumentation system that is adaptable to the needs of a wide variety of situations is based on fluorescing materials. The thermal dependence of fluorescent thermometry may be exploited to provide for emissivity-independent, contact or non-contact, optical alternative to other more conventional techniques, e.g., those employing pyrometry, thermocouples or thermistors. There are certain situations in which the advantages of fluorescence based thermometry over other methods make it the only useful approach.

The motivation of this research is two-fold. The first is to meet the recent increasing needs for temperature sensors capable of operating accurately and reliably in harsh environments, such as coal-based power generation and distribution industries,
nuclear power industries, glass and metal manufacturing/processing industries and other high temperature chemically corrosive environments. The second motivation of this research is to make accurate measurements of surface temperatures. In general, optical sensors offer many advantageous features over conventional electrical sensors for applications in harsh environments. These include: immunity to electromagnetic interference (EMI), resistance to chemical corrosion, high sensitivity, large bandwidth, capability of remote operation, small size, light weight, absence of ground loops and capability of operation at high temperatures [1,2]. These advantages have promoted worldwide research activities in the area of optical fiber sensor technologies for harsh environments.

The sensor prototype developed in this research is intended for non-intrusive, direct temperature measurement, in the primary and secondary stages of slagging gasifiers and the precise measurement of surface temperatures. These gasifiers are used in the coal-based power generation industries, where a sensor is required to withstand extremely harsh environments imposed by high temperature, high pressure and corrosive chemical materials. In this research, innovative techniques are presented for high temperature sensors capable of operating at temperatures up to 1600°C. These sensors fulfill the need for real-time monitoring and long-term direct measurement of high temperatures in extremely harsh environments. The efforts devoted to innovative sensing techniques focus mainly on the following issues: 1.) Fabrication material selection and structure design of probe. 2.) Optimization of sensor prototype and performance evaluation. 3.) Sensor prototype implementation.
1.2 **Scientific and Industrial Needs for Novel Temperature Sensors**

The majority of commercially available temperature measurement instruments are made using only a few basic types of devices: thermocouples, resistance thermometers, liquid-in-glass thermometers and radiation thermometers. These traditional measurement instruments have been in use for many decades. The major sources of their instability or drift, as well as possible systematic errors, are well understood. As temperature sensing technology matures, many traditional techniques are still unsuitable for specific measurement requirements.

Conventional temperature measurement sensors are generally inexpensive while being widely available for scientific and industrial applications. Innovation and research and development activities in temperature measurements need to be pursued to enhance the performances attainable by traditional techniques concerning measurement sensitivity, accuracy, response time and range limitations. Temperature measurement requirements necessary in today’s modern industrial environments include monitoring surface/internal temperature profiles, measurements in hostile environments and gas temperature measurements. All of these environments entail non-intrusive temperature acquisitions in which the sensor does not affect the medium of interest.

One representation of a harsh environment is an entrained flow slagging gasifier, which is one of the main units among coal gasification facilities. In the new emerging coal-fired power plants for advanced power generation, the coal gasification technique [3] has been developed to generate electricity and other high-value energy products without extremely harmful byproducts. Rather than burning coal directly, coal gasification reacts coal with steam using carefully controlled amounts of air or oxygen under high
temperatures and pressures. Hot exhaust from the gas turbine is then fed into a steam
turbine, producing a second source of power. This unique integrated gasification
combined cycle (IGCC) configuration of turbines offers major improvements in power
plant efficiencies compared with conventional coal combustion. To optimize
performance for these IGCC plants, certain relevant physical parameters should be
monitored and controlled precisely for coal gasification processes, such as real-time
accurate and reliable monitoring of temperatures at various locations in a coal gasifier,
pressure distribution monitoring, burning material flow patterns inside the gasifier, air or
oxygen monitoring, etc.

The accurate continuous monitoring of the interior temperature at several strategic
locations enables the timely adjustments of the input streams for an optimum
performance. Prevailing harsh conditions of high temperature, high pressure and reactive
constituents within the gasifier make extraordinary demands on the temperature sensor.
The gasifier must be operated at a temperature high enough for the ash in the fuel, such as
combustion, to melt and become sufficiently fluid to flow out of the gasifier through the bottom
tap-hole. Load changes will also affect the temperature in the gasifier and downstream,
which would require adjusting the operating conditions. Operating under the optimum
temperature would cause the molten slag to become viscous or solidify, plugging up the
tamp-hole and preventing additional slag from draining out of the gasifier. Eventually
the gasifier has to be shut down, cooled off; and the slag, now in the form of a hard
vitreous rock, has to be manually chipped out to be removed from inside the gasifier.
The shut down to clean up the slag may take weeks, resulting in a lengthy loss of
production. Operation above the optimal temperature would significantly shorten the
lifetime of the refractory lining. In addition, more of the alkali species in the ash would be volatilized, reacting with the ash particles entrained in the gas to form low temperature eutectics which deposit in the cooler sections of the gasifier or downstream equipment, such as the boiler, causing plugging problems. Exceeding the operating temperature will also reduce the conversion efficiency of the gasification process in the production of the synthesis gas.

In order to realize the full economic potential of the gasification systems, there is an increasing need to utilize a wide variety of feedstock in addition to coals, such as biomass, refuse, wood wastes, etc. in the gasification plants. The ash properties of these various feedstocks vary significantly, and would thus require operating the gasifier at different temperatures to facilitate slag tapping. The flow condition inside the gasifier is highly turbulent, with many pockets of gas recirculation zones. Temperature in various regions of the gasifier could be widely different. The temperature at the exit of the burners could be above 1927 °C (3500 °F), where as close to the wall temperatures could drop to less than 1316 °C (2400 °F). Real-time accurate and reliable monitoring of temperatures at various locations in a gasifier is thus highly desirable.

Various methods for measuring temperature in harsh environments have been investigated in the past [4-8]. Among these are optical and acoustical pyrometers, and high temperature thermocouples. However, due to the stringent surroundings involving entrained molten slag, typical temperature sensors and measurement devices are very difficult to apply [9-13]. At present, retractable thermocouples protected by thermowells are being used for gasification systems. Due to decalibrations of the thermocouple and corrosion of the thermowell, the total exposure time of the sensor probe is limited to only
a few days to a few weeks. Decalibrations which are caused by the diffusion of impurities into the thermocouple junction at high temperatures, is an inherent problem. This makes thermocouples unsuitable for extended deployment even if the thermowell corrosion problem can be overcome.

Non-contact optical pyrometer applications involve an infrared transparent high temperature window on the gasifier wall to maintain a large pressure differential, while allowing transmission of the infrared radiation emitted by the product gases to the detector placed outside the gasifier. Obstruction of the sight-path opening for the pyrometers in the refractory wall by molten slag is a major problem. Shifting of the refractory lining, which could have a thickness of 2 feet or more, during heat-up and operation processes could also cause blockages of the sight-path. In addition, the measurement is also subject to interference from the radiation emitted by entrained particles or the relatively cold refractory walls.

Direct contact temperature measurement is preferred since it will give the measurement for the specific location of interest. Several of these devices installed at the critical locations inside the gasifier could thus provide the temperature profile, and performance of the gasifier could be monitored and improved by making adjustments in a timely manner. However, no direct contact measuring devices are available to date due to material issues. The highly corrosive molten slag attacks both metals and ceramics. Ceramic materials are also susceptible to attack from alkali vapors in the gas [14-18]. This situation suggests for innovative techniques that can operate in gasifier harsh environments for real-time, reliable monitoring of temperature to be developed.
Another prevailing challenge in thermometry involves the precise measurement of surface temperatures. Radiometry is currently the most conventional means in the noncontact technique while being highly unreliable unless the emissive properties of the surface are highly characterized. When this technique is used emissivity and reflection errors result, then the apparent and not the actual temperature is indicated. The second objective of the proposal is to demonstrate the ability of a fluorescence-decay-rate (FDR) fiber-optic temperature sensor to measure surface temperature with high accuracy when operated in a thermally compensated mode.

1.3 Requirements for Temperature Sensors in Coal Gasifiers

For optical temperature sensors to be useful in coal gasifier environments, there are several requirements that must be met. The operating temperature in the coal gasifier is in the range of 1200°C - 1600°C, depending on the physical locations in the chamber. The high temperature is the main reason most electronic sensors are inapplicable. Some optical sensors cannot be deployed because of the limitations of the thermal properties pertaining to the fabrication materials used. For example, silica optical fibers can only withstand temperatures up to 800°C before the dopants start to thermally diffuse. To measure high temperatures accurately in a wide measurement range with high resolution, proper fabrication materials are essential, as well as a simple and stable mechanical structure of the sensing probe. Pressures as high as 500 psi can be encountered in the gasifier chamber. In order to be able to survive in such high pressure environments, the optical temperature sensing probe must be constructed and fabricated with ample
mechanical strength while having its optical paths entirely sealed to provide the necessary protection.

Optical temperature sensors for volatile environment sensing applications must be thermally stable. Temperature related degradation mechanisms, such as thermal shock, thermal cycling, thermal stress, and thermal fatigue from high heat fluxes, must be considered in the elevated temperature sensor design for long term stable measurements. Rigorous mechanical structures and special fabrication materials are crucial to promote the thermal stability and deployability. These sensors must be capable of remote operation and be flexible enough for easy deployment. Features such as mechanical vibration-proof, high mechanical strength, and remote monitoring and control capability are thus inevitable.

With temperatures exceeding 1200°C, pressures exceeding 500 psi, and chemically corrosive agents such as alkalis, sulfur, transition metals and steam, it is hard to find a material that is impervious to such an extensive corrosive attack. Conventionally, commercially available temperature sensors exhibit greatly abbreviated lifetimes due to the hostile environment. Proper fabrication materials are needed to implement the sensing probe to be chemically corrosion resistant. In addition, the sensors are required to have self-calibration capability so that the guiding fiber loss variations and the source power fluctuations can be fully compensated.

As the market for optical temperature sensors for harsh environment grows rapidly, the cost of the sensors and instrumentation is becoming a concern of increasing importance. In order to achieve successful commercialization, optical temperature sensor systems must be robust as well as low cost. This requires that the complexity of the
sensor system is kept to the minimum and the technique and process of fabricating sensor probes have the potential of allowing mass production.

1.4  

Requirements of Temperature Sensors for Surface Measurements

Any apparatus brought near to, or in contact with, the source-body surface changes the heat-transfer rates between the surface area and its environment. The rates of surface chemical reactions, evaporation, and condensation may be similarly affected. To obtain high accuracy in the contact mode, the temperature sensor has to be fused onto the surface by cement or inserted into a well drilled in the sample. The lack of such measures results in probes with accuracies no better than 5-10% [19].

The first error in surface measurements stems from the actual area of contact that is generally a small fraction of the apparent contact area because of the surface roughness of the source-body to be measured, generating a layer of high thermal resistance between the sample and the probe. The probe itself may cause thermal perturbations at the point of contact on the source-body to be measured. The result of this blanketing or thermal damming is that the temperature to be measured is altered by the means of measurement causing large inaccuracies in surface temperature measurements. The proposed FDR temperature sensor will avoid these problematic issues that have lingered for decades.

1.5  

Review of Non-Optical Based Temperature Measurement Devices

In science and technology, temperature is defined in terms of the amount of heat transferred in a Carnot cycle [20]. This is not the most practical way of measuring temperature, and in practice many different techniques are used depending on the
temperature measurement requirements. In practice, every temperature measurement involves the use of certain calibrated transducers to convert a measurable quantity into a temperature value. These transducers to convert changes in the temperature into other measurable physical quantities, such as electromotive force (thermocouple), volumetric expansion (liquid thermometer), resistance (resistance temperature detector-RTD), radiated energy (radiation thermometer), dimensional change (bimetallic thermometer), or some other characteristics of a material that varies reproducibly with temperature [21,3]. For high temperature measurements in excess of 1000 °C, the existing non-optical measurement techniques are very limited. Possible choices include high temperature thermocouples and acoustic methods.

1.5.1 Electrical Thermometry

The most universal electrical temperature sensors found in society today detect deviations in resistance or voltage with temperature. Resistance thermometry is an electrical method that is based on the variation of resistance for temperature measurements. A resistance thermometer makes use of the change of resistivity in a metal wire with temperature. As electrons migrate through a metal, the thermal vibrations of the atoms in the crystal lattice impede them. The impedance and resistivity are both proportional to temperature and thus temperature dependent. This effect is very marked in pure metals. Resistance thermometers are usually more sensitive than other electrical temperature sensing devices but operate over a smaller range (248 K - 1125 K). Potential limitations for these devices are caused by alterations in lead temperature and excess power to the circuits [22].
Thermocouples are the most common electrical thermometry device used to make temperature measurements. These devices depend on the principle of the Seebeck effect: when a conductor is placed in a temperature gradient, electrons diffuse along the gradient and an electromagnetic field (emf), or thermovoltage, is generated. The magnitude of the emf depends on the material and also on its physical condition. To measure the generated thermal emf, the circuit must be completed using a second different conductor to form a common junction. The thermocouple emf is then the difference between the emfs generated in the two conductors. The voltage between the wires is proportional to the ambient temperature. These devices typically operate in the range of 225 K - 1975 K, varying depending on the type of thermocouple used.

Figure 1.1: Nickel-chromium vs. nickel-aluminum thermocouple diagram.

Standard tables show the voltage produced by thermocouples at any given temperature, so for example in the above diagram Fig. 1, the K type thermocouple at 300°C will produce 12.2mV. Unfortunately it is not possible to simply connect up a voltmeter to the thermocouple to measure this voltage, because the connection of the voltmeter leads will make a second, undesired thermocouple junction. To make accurate
measurements, this must be compensated for by using a technique known as cold junction compensation (CJC). The output from thermocouples is small which makes them not immune to error. Typical outputs are of the order of millivolts to tens of millivolts. The major limitation in the use of thermocouples for precise thermometry arises from the fact that unwanted emfs are generated in inhomogeneous thermoelements passing through temperature gradients.

The useful temperature range for a particular thermocouple is somewhat arbitrary. One can argue that the upper limit is determined by the melting points of the thermocouple materials, but in practice the useful upper limit is usually well below the melting point and depends upon such factors as operating time at elevated temperatures, environment, thermoelement diameter, and the exact conditions of use. The lower limit is also somewhat arbitrary, but it is usually determined by impractically small thermopower.

There are numerous types of thermocouples available, which are formed by different metals. Eight types of them are standardized [21], including T, E, K, J, N, B, R, S type thermocouples. Different types of thermocouples are characterized to measure up to certain levels with different resolutions. For high temperatures over 1000 °C, Type B, R, S thermocouples are commercially available. In chemically corrosive environments, high temperature thermocouples that utilize precious metals are used and have a limited life of only a few days due to their susceptibility to attack from corrosive chemicals. They drift significantly under high temperature environments for long-term operation and are susceptible to decalibrations due to diffusion of impurities into the thermocouple
junction at high temperatures making them unsuitable for extended deployment in harsh environments.

Resistance temperature detectors (RTDs) make use of the fact that resistance to flow of electricity in a wire changes with temperature. Platinum is the most commonly used wire material. Wirewound and thin film RTDs are two types of RTDs normally found commercially today. Wirewound RTDs consist of wire wound on a bobbin, which is enclosed in glass. For thin-film RTDs, a film is etched onto a ceramic substrate, and sealed. RTDs are more accurate and stable than thermocouples, but cannot be used to monitor extremely high temperatures. One limitation to impact RTDs on thermocouples has to do with application. RTDs do not function properly at temperatures greater than 650 °C [22]. Therefore, in certain industries and extremely high temperature applications such as heat treating, oven control, jet engine testing, steel making and metal fabrication, RTDs cannot be used. The exotic metals platinum and tungsten thermocouples will continue to dominate in these high temperature applications for the foreseeable future of electrical thermometry.

Like RTDs, thermistors also change resistance with changing temperatures, but they are more sensitive than either RTDs or thermocouples. Thermistors change their resistance much more significantly than RTDs with changing temperature. However, this change is highly nonlinear. Due to their extreme sensitivity and nonlinearity, thermistors are limited to measuring temperatures of a few hundred degrees Celsius. They are less rugged than RTDs, further limiting their application.
15.2 Acoustic Methods

It is well known that the speed of sound in a material depends on the temperature [23,24]. Temperature can thus be measured by detecting the speed of sound that propagates inside a material. This technology is especially useful for measuring gas temperature in a combustion chamber, where it is difficult to measure the temperature using inserted probes due to low thermal mass and low conductivity of gases, and the strong radiation coupling of the walls of the enclosure to the sensor at high temperatures. Using the gas itself as a temperature sensor overcomes these problems.

The prevailing difficulty with acoustic methods derive from the speed of sound being strongly dependent on the composition of the gas along the path, which is generally not homogeneous in the combustion chamber. Soot particles slow the acoustic wave significantly, and will result in large error. Furthermore, a dilemma arises from the refraction of the sound wave front by the density and temperature gradients in the chamber. These are often turbulent which distort the wave fronts, making the accurate determination of time of flight problematic. Since the sound wave travels with the gas, the apparent speed of sound will also be strongly affected by the flow velocity through the Doppler effect. Practical systems usually attempt to compensate for this effect by performing measurements in both directions. High temperature measurement uncertainties up to 30 °C at 1000 °C have been claimed for this method [25].

1.6 Review of Optical Based Temperature Measurement

Optical sensors are devices in which optical signals are transformed in a reproducible way by an external physical stimulus such as temperature, strain, pressure,
strain, etc. An optical beam is characterized by several variables, such as variation with
time, intensity, spectrum, phase and state of polarization. Many different physical
phenomena related to these characteristics are used to perform sensing functions.

Temperature sensors probably constitute the largest class of commercially
available optical sensors. Besides bulk optics based sensors, a wide variety of
temperature sensors using fiber optics have been developed [26]. They offer numerous
significant advantages over electric sensors, such as small size, light weight, immunity to
electromagnetic interference, etc. The main existing techniques for optical thermometry
are remote pyrometers, thermal expansion thermometers, fluorescence thermometers, and
thermometers based on optical scattering including Raman and Raleigh scattering.

1.6.1 Distributed Temperature Sensors

The interaction of light and the lattice vibration when light is incident on a
substance causes a change in the energy level of the lattice vibration and a shift in the
energy of the light that is scattered. This leads to scattering of light with a different
wavelength from that of the incident light. This phenomenon is called Raman scattering,
and the two components of the differing wavelengths are termed Stokes light and anti-
Stokes light.

The method used in fiber optic distributed temperature sensors is based on the fact
that the intensity of the light components generated by Raman scattering when a light
pulse is propagated through a body composed of optical fibers depends on the
temperature of that body [27]. This makes it possible to determine temperature
distribution via Raman scattering intensities generated at various points along the optical
fiber path. The temperature measurement range of the fiber optic distributed temperature sensor was narrow at 223 K to 423 K using conventional optical fibers, thus limiting the objects that could be measured.

Later versions of this sensor were able to detect up to 873 K with an accuracy of 0.1 K [27]. The utmost limitation of these sensors are derived from optical losses. When optical loss increase is equivalent in the two components of the Raman scattering light, the accuracy of the measurement is not affected, but the distance at which measurement is possible decreases. However, if the optical loss increase of the two components differs, both measurement distance and accuracy suffer.

Spontaneous Brillouin scattering based systems are also temperature dependent and provide a signal that is an order of magnitude greater than Raman scattering. Brillouin scattering in optical fibers result from the interaction between the incident light beam and thermally generated acoustic waves in the fiber. The advances in narrow bandwidth pulsed laser technology and low loss optical fibers have allowed the Brillouin signal to be separated from the Rayleigh signal. Brillouin scattering offers considerably increased range beyond the limit of the spontaneous Raman based sensor with the possibility of 3 K resolution [28].

1.6.2 Remote Temperature Pyrometers/Radiation Thermometry

Radiation thermometry devices are typically used for extremely high temperature measurements where other devices would be destroyed. This method utilizes modern imaging optics and detectors to measure the flux created by a hot object or environment. Radiation thermometry makes use of the fact that all objects emit radiation in the infrared
and visible parts of the spectrum, the intensity of which varies strongly with temperature. As the temperature of the perfect or ideal radiator known as a blackbody increases, radiation is emitted at all wavelengths in a continuous manner. The radiometer senses radiant flux from the target and generates an output signal which, through a calibration algorithm, is used to provide a measure of target emissivity of the surface. The emissivity is a parameter that is complementary to the spectral reflectance of that particular surface.

Radiometers have various origins that cause inaccurate temperature measurement readings. In practice, the target seldom approximates a blackbody radiator and the target environment, comprised of its surroundings and the atmosphere in its line-of-sight, is not as well controlled as during the calibration process. Temperature measurements by these devices are affected by an object's emissivity. Most organic materials and painted surfaces have an emissivity of approximately 0.95 (the standard preset in fixed emissivity units) [29]. Inaccurate readings result, however, when measuring shiny or polished metal surfaces. Radiance temperature tends to be less than the true temperature and a correction needs to be applied for sources with emittances that differ from 1.0 to achieve an accurate temperature measurement. The error associated with this method can be as much as 44% for $\varepsilon = 0.1$ [30].

All materials with temperatures above absolute zero degree emit electromagnetic (thermal) radiation and the amount of thermal radiation emitted increases with temperature. The measurement of the amount of thermal radiation emitted by a material can therefore be used as an indicator of its temperature. The basic operating principle of radiation thermometers is to measure part of thermal radiation emitted by an object and
relate it to the temperature of the object using a calibration curve that has been
determined either experimentally or theoretically (from Planck’s law) [29]. Typical
radiation thermometers measure temperature above 600 °C and dominate the temperature
measurement market for temperatures up to 2000 °C. The main problematic issues for
these devices involve field of view issues.

1.6.3 Interferometric Temperature Sensors

Interferometric fiber optic sensors are a large class of extremely sensitive fiber
optic sensors and are applicable for measuring almost any physical quantity. They are
typically used when ultra-high sensitivities are required and/or in applications of
localized measurements, although sensor lengths longer than one meter are sometimes
possible. This sensing technique is primarily based on detecting the optical phase change
induced in the light as it propagates along the optical fiber.

Fiber optic interferometers are generally intrinsic sensors in which light from a
source is equally divided to follow two (or more) fiber-guided paths. The beams are then
recombined to mix coherently and form a fringe pattern that is directly related to the
optical phase difference experienced between the different optical beams. The phase
difference can be measured by counting the fringes, and then transformed into a physical
dimension change that gives information about the temperature. The most common
configurations of the interferometers are the Mach-Zehnder and the Michelson fiber optic
sensors [31].

The Fabry-Perot (FPI) sensor published by Lee and Taylor in the early 1990s
discussed an example of another fiber optic temperature sensor based on interferometry
They have later described improvements [33]. This work described the use of a light emitting diode (LED) as a low coherence light source. The sensor uses two Fabry-Perot interferometers in series, one for sensing and one for reference. The optical output from the LED is spectrally modulated by reflection from the sensing FPI. Then, reflection or transmission by the reference FPI produces an interferometric beat response similar to that observed when a laser is used with the sensing interferometer alone. This particular design was only operable up to 575 K due to the degradation in fringe visibility with increasing optical path length difference. Other literature reports a reflectively monitored Fabry-Perot temperature sensor characterized with the capacity to measure a maximum temperature of 1320 K [34].

1.6.4 Fiber-Optic Fluorescence Decay Rate (FDR) Temperature Sensors

Although various devices may be used for the purpose of measuring temperature in science, sensors based on optical fibers have become widely recognized as a convenient and practical tool in remote, inaccessible spaces, in harsh environments where electromagnetic/radiofrequency interference is relatively significant and where accurate measurements are required [35]. Historically in many instances, temperature sensors based on glass fibers were employed. However, the limitations imposed by glass based temperature sensors lead to the search for more robust and stable systems on other high temperature materials. Majority of the glass based thermometric systems were limited by their intrinsic material properties to temperatures less than 400 °C, in general, while others based on silica fibers may be used intermittently up to approximately 1000 °C. For many applications temperature measurements are needed well beyond 1000 °C,
making the conventional fiber optic sensors unsuitable for deployment. Hence, appropriate replacements have been sought for this important temperature region and are presented in this work.

Single crystal fibers have rather remarkable properties which have led to their use in numerous optical and structural applications. Although, the bulk of such applications have largely been in the areas of nonlinear optics, solid state laser devices, modulators, amplifiers, high power beam delivery and beam delivery in medicine [36]. These fibers have been employed in specialized fiber optic sensing applications where their optical and mechanical properties are superior to those of glass based materials [37-39]. Single crystal fibers exhibit few or almost no internal defects, offering the possibility of high crystalline perfection and near-theoretical strength [40]. While early work on fiber optic rare earth based thermometry employed Nd$^{3+}$ doped glasses and crystals whose fluorescence decay lifetimes were measured as a function of temperature [38,39], these were not found suitable since such fibers exhibited non-monotonic decay times over the entire temperature range investigated.

1.6.4.1 Historical Foundations on Fluorescence Decay Type Temperature Sensors

Suggestions on the use of phosphors for thermometric applications by Neubert date back to as early as 1937 [41]. During the later 1940’s and early 1950’s Urbach contributed to developments and approaches pertaining to phosphor thermometry. In 1952 Bradley [42] presented one of the first thermometric applications by measuring the temperature distribution on a flat wedge in a supersonic flow field using a phosphor
granted by Urbach. U. S. Radium Corporation later marketed this thermometric phosphor technology by work from these pioneers.

The advent of the ruby laser by Maiman in 1960 used the efficient fluorescence of ruby, in which Cr$^{3+}$ is the activator in an Al$_2$O$_3$ host. Its temperature dependent fluorescence properties have also been applied to thermometry in numerous journals [43-47]. Various trivalent rare earth impurities are now used, particularly Yb$^{3+}$, Tb$^{3+}$, and Er$^{3+}$ in a variety of hosts. This led to continuing progression of technological tools during the 1970’s for exploiting the thermal properties of phosphor emission in a broader range of applications. Examples include high quality optical fibers capable with high transmission properties. By applying the phosphor to the tip of an optical fiber, Wickersheim and Alves [48] produced the optical analog of a thermocouple. Their design featured prefiltration of UV excitation radiation by reflection from series of dichroic mirrors covering a temperature range of 9 °C to 250 °C. In 1979, several other methods were presented including the extraction of temperature from phosphor time decay [49].

Sholes and Small reported only the principle of the fluorescent decay thermometer for biological applications using a ruby crystal as the active medium. The device relied upon single shot measurements using a tungsten source modulated by a mechanical camera shutter to excite the material at 10 ms intervals. The time constant in this particular sensor was a monotonically decreasing function of temperature over the range from about 200 K to 400 K with a resolution of 0.3 K [50]. For high temperature applications, above 575 K, conventional sensor binder and adhesives and the optical fiber buffer and jacket materials suffered from thermal degradation.
McCormack produced the first working fiber optic temperature sensor based on fluorescence in 1981, which again relied upon lamp excitation (250 W halogen lamp) with mechanical modulation using barium chlorofluoride activated by divalent samarium as the active medium. The material produced a narrowband emission with high quantum efficiency, however the decay rate was not a monotonic function of temperature [51].

The first monolithic all crystalline fiber optic temperature sensor was reported in 1996 [52]. Both the fiber and the sensing element were made of crystals in this novel construction. This approach allows the sensor to operate to the melting point of the fiber, which is approximately 2200 K for YAG. The probe that was tested consisted of an Er:YAG transducer tip that was pumped with a tunable Ti:Sapphire laser with 10 ns output pulses at 790 nm. This system was operable in the temperature range of 300 K to 1000 K with a temperature uncertainty of approximately 3 K.

One recent thesis by University of South Florida graduate student, Dameon Henry, reported the first direct measurement of molten aluminum with an all-crystalline fiber optic sensor consisting of a single-crystal YAG (Y₃Al₅O₁₂) lead fiber and an Er:YAG tip. The sensor described in this work was tested previously to 1000 K [30] before being extended to the highest temperature ever recorded for a fiber optic temperature sensor at 1520 K and successfully measuring the temperature of a molten conductor [37]. The sensor relied on the dependence of the fluorescence decay rate on multiphonon relaxation of the impurity ions within the host crystal. This relaxation was dependent on temperature as well as the energy gap between the fluorescent and terminal levels. A theoretical curve was fit to the data using physical parameters of the transducer material,
and was distinctive in that it revealed electron coupling to a second phonon mode at high temperatures for the first time in any material.

Another recent thesis by University of South Florida graduate student, Russell Van Cleave, reported an all-crystalline fiber optic sensor consisting of a single-crystal YAG lead fiber and an Yb:YAG tip demonstrating maximum temperature measurements of 1700 K with a sensitivity of 0.01 /K at 1300 K [53]. This work represented the highest temperature measured by a fiber optic transducer at that time, with the previous record at 1520 K.

New reports have cited fiber optic temperature sensors based on fluorescence decay using monolithic crystalline construction using Er:YAG and Yb:YAG phosphors to reach as high as 1,900 K while addressing the future envisioned developments of this type of sensor [54]. The authors have also reported results which suggest that the temperature dependence of phonon assisted energy transfer is well described by the electron coupling to optical phonon modes at the two extremities of the phonon spectrum [55].
CHAPTER 2

ELEMENTARY PRINCIPLES OF FLUORESCENCE DECAY RATE (FDR) THERMOMETRY

It has long been generally known that the fluorescence of a material is temperature dependent. There are numerous ways in which this temperature dependence is manifested. Fluorescence typically corresponds to weakly allowed transitions between electronic levels of the phosphor. The material emits light because there may be no other way for the electron, once excited by incident radiation, to give up its energy and return from the metastable fluorescent state to the ground state. A variety of competitive processes, some radiative and some nonradiative, exist. Hence all phosphor materials can be expected to exhibit temperature dependent decay time over some temperature interval. Since a number of determinants underlie the intrinsic nature of the fluorescence process, we begin with a concise overview of it.

2.1 The Fluorescence Process

The fundamental aspects of the fluorescence of solid materials are well understood. Prior to excitation, an active ion’s electrons occupy only the thermally accessible states according to the Boltzmann distribution. A means to deposit energy in the material is required in order to excite a higher electronic state. This may be attained by exposure to electromagnetic radiation (visible, ultraviolet, x-ray beams, etc.), particle beams (electrons, neutrons or ions) or electrical current as is the case for semiconductors.
The atomic configuration will not typically remain permanently excited but will either return to its ground state or assume an intermediate level. Conservation principles dictate that the amount of energy absorbed must also be released. This may be manifested by emission of a photon with energy equal to that of the energy level difference, by transfer of energy via quantized vibrational (phonons) exchange in the material, or by more complicated energy exchange mechanisms involving numerous processes.

Many of the materials found to fluoresce efficiently are those for which the fluorescence originates from a deliberately added impurity. As an example, a host material such as Yttrium Aluminum Garnet (YAG, Y$_3$Al$_5$O$_{12}$) is transparent and nonfluorescent until rare earth impurity ions such as Ytterbium (Yb$^{3+}$) are added. It then fluoresces with properties that make it useful in the design of thermometry systems. The dopant concentrations are usually on the order of a few percent or greater.

Fluorescence as referred to here is the emission occurring from electronic transitions and is usually in the visible, near infrared (NIR) as for ytterbium, or the ultraviolet (UV) spectrum. An impurity ion in a crystal may be represented by a configurational coordinate curve as in Fig 2.1. Let us assume that the ion is in its ground electronic state and its lowest vibrational state; temperatures below 70 K generally produce such a situation. A transition upward from A to B may be induced by the absorption of a photon of energy ($E_B - E_A$). The impurity will then be brought to the excited electronic state and to an excited vibrational state level of this state. As a consequence of the Franck-Condon principle, which states that atoms do not change their position during an electronic transition, the coordinate of the center, immediately after the absorption has taken place, is the same as the coordinate before the absorption. After the
absorption, the center will tend to transfer its vibrational energy to the lattice and nonradiatively decay to the lowest vibrational level designated by $C$. From this level the center will further decay to level $D$ of the ground electronic state, giving up the energy $(E_C - E_D)$ as fluorescent radiation. From $D$ the center will then decay to its lowest vibrational state. The difference in energy between the absorbed photon and the energy of the emitted photon is called Stokes shift.

The energy level diagram shown in Fig. 2.2 can be used to represent a fluorescent ion in a host lattice. The incident light excites ions from the ground state 1 to an excited state represented by the absorption band 3. The ions then decay by a fast radiationless transition to the metastable state 2. From this fluorescent level the ions decay to the
ground state by purely radiative process and by other processes that we may call secondary (nonradiative).

It is typically valid that the fluorescence spectral properties of any material will alter with temperature. This is so in part due to the Boltzmann distribution governing the partitioning of the populations in various participating vibrational levels of the ground, excited, and emitting states. A change in the intensity distribution results since oscillator strengths vary in accordance with selection rules and the Franck-Condon principle. The temperature dependence of these processes can be striking when there is competition with states which contend between radiative and nonradiative deexcitation pathways. The rate of change for the population of the emitting state, \(2\), to a ground state, \(1\), is the sum of constant purely radiative spontaneous emission \(A_{1,2}\), and a nonradiative component, \(W_{1,2}\), which is temperature dependent. The measured lifetime \(\tau\) (in s) is given by the following expression:

\[
\tau = \frac{1}{R(T)} = \frac{1}{A_{1,2} + W_{1,2}}
\]

where \(R(T)\) is the measured decay rate in units per second.

2.2 **Elements Altering the Fluorescence Process of Rare Earth Impurity Ions in Crystals**

There are many influences that have been found to alter the fluorescence for rare earth impurity ions in materials resulting in an enhancement or degradation in the fluorescent process of interest. One must take into account careful consideration of these elements to be able to achieve the optimum results when using the fluorescent decay time as the correlator for temperature measurements.
2.2.1 Rare Earth Impurity Ion Concentration

The parameters determining the fluorescence characteristics of any given phosphor are dependent on the concentration of the activating rare earth impurity ion. Overall decay time, intensity, relative spectral distribution, rise time, and response to temperature are all affected to some degree by the rare earth impurity ion concentration. Typically the more rare earth impurity ions in a host material, the more it will fluoresce, up to a certain point. However, when the concentration levels reach a certain limit, another nonradiative deexcitation pathway becomes important. As the activator density is increased, the probability that an excited activator will transfer its energy nonradiatively to a neighboring dopant ion increases. The onset of this process is usually referred to as concentration quenching. For other dopants, even when in the same host material, the optimum concentration that produces the maximum intensity will be different [56,57].

One typically seeks to maximize the intensity of the phosphor for thermometry applications. However, there are other considerations that may warrant the use of different strategies. For example, at high concentration the fluorescence decay profile may not be one of a simple exponential form. This is important for decay time based thermometry since multiexponential and nonexponential decay profiles are difficult to interpret. Complex waveforms make calibration and data analysis extremely difficult and at times intractable.

The spectral emission distribution also can be sensitive to impurity dopant concentrations. Literature has illustrated this spectral emission dependence on
concentration doping for Eu:Y$_2$O$_2$S [58]. They indicated that the $^5$D$_2$ emission of Eu is especially sensitive to the Eu dopant concentrations.

2.2.2 Effects of Saturation

High incident fluxes from any excitation source may lead to fluorescence saturation effects. Phosphor efficiency changes as a function of incident flux when this occurs. Above a certain threshold value, overall intensity decreases, but for a lower dopant concentration this threshold value itself is lower and the rate of decrease is faster than at higher dopant concentrations. Literature cites the increasing of electron beam voltage, independently of beam current, will degrade the saturation of the phosphor according to Yamamoto and Kano for Yb:Y$_2$O$_3$ [59]. Conversely the situation may improve for some phosphors as cited in literature by Douling and Sewell in the case of ZnS and Zn$_2$SiO$_4$ [60]. Saturation is itself a temperature dependent phenomenon.

Diminishment in the fluorescence decay time with increasing laser fluence has also been described in literature [61]. Imanaga et al. suggests several possible mechanisms that may cause fluorescence saturation behavior in this instance. In many situations the dominant mechanism of these saturation effects is beam induced temperature rise. To determine whether beam related effects will be a problematic issue for any given situation, experimental results and studies would have to be pursued for each particular circumstance. Typically one does not have situations in which they deliver an excess of laser excitation due to complexities in transporting beams over long distances. Optical fibers customarily are the waveguides of choice for transporting the beams and have limited fluence handling capacity for guiding the beams.
2.2.3 *Host Lattice Associated Impurities*

Inevitable amounts of undesired species in a host material may be detrimental in phosphor efficiency for thermometric applications. These impurities may change the atomic electronic environment experienced by the activators so as to either augment or hinder phosphor performance. Typical characteristics of impurities include a decrease in the emission intensity at fluorescence wavelength of interest. This is due to the impurities absorbing at wavelengths similar to those of the typical, thus effectively stealing excitation energy and decreasing the number of excited fluorescent centers. Furthermore, nonradiative energy transfer from an excited activator to such impurities may be efficient, thus increasing the decay rate and quenching the emission. In fluorescence decay thermometry, increasing the rare earth impurity dopant concentration of the fluorescing ion is plausible to decrease lifetime, thus enhancing the sensitivity of the temperature sensor.

2.2.4 *Interactions of Different Rare Earth Impurity Ions*

The quenching or enhancement of the fluorescent output of a crystal containing a certain type of rare earth impurity ion is often observed when another type of impurity ion is added into the host crystal. If this second impurity ion presents a relevant absorption spectrum in a region in which the pumping source is emitting strongly and the energy absorbed by it is transferred by some mechanism to the fluorescent ion, an enhancement of the fluorescence may result. The opposite effect may take place if, given a certain fluorescent ion, another ion is added to the crystal with no relevant absorption band but with one level coupled to the metastable level of the fluorescent ion. If the
additional ion is not fluorescent or is fluorescent with some low efficiency, a reduction of the fluorescence output will result.

There are two basic mechanisms that may induce energy transfer between rare earth impurity ions in crystals. The first is the mechanism by which energy transfer between an ion S and an ion A takes place in a cascade type, namely by emission of photons by the ion S and reabsorption of photons by ion A. In this case the ion S must be, by itself, a good emitter of fluorescence in a region in which the ion A absorbs strongly. In this case the lifetime of the fluorescence of the ion S is not affected by the presence for the ion A and the emission of fluorescence by S shows a decrease only in correspondence to those wavelengths at which ion A absorbs.

Another possible energy transfer mechanism may be the resonant type, which produces what is known as sensitized fluorescence, wherein the additional doping ion that provides the enhancement of the absorption features of the phosphor is called the sensitizer and the codopant ion is called the activator which may decay radiatively or nonradiatively. The activator will exhibit strong absorption providing there is efficient spectral overlap between its absorption spectrum and the emission spectrum of the sensitizer ion. In the present case the lifetime of the sensitizer, if measurable, is found to decrease in the presence of the activator. Subsequently all the fluorescence emission of the sensitizer originating in the state participating in the energy exchange is quenched as a function of the activator doping concentration.
2.2.5 Rare Earth Impurity Ion Particle Size Effects

Literature has noted a change in fluorescence lifetime with a change in the size of the dopant impurity ion of interest [62]. An example of this has shown an increase from 436 μs to 598 μs for a decrease in particle size from 0.42 μm to 0.11 μm, respectively. This suggests that the fluorescence decay time of any phosphor will be the weighted average composite of the individual decay lifetimes arising from the distribution of impurity ions particle sizes. The quantum theory of decay rates of electric-dipole emissions explains the observable deviations of decay rate as a function of particle size. It predicts that the spontaneous lifetime of fluorescence is inversely proportional to the index of refraction of a fluorescent material [62]. The index of refraction $n_c$ in the proximity of an ion isolated in a crystal will differ from the index of refraction of the same ion $n_s$ with a different particle size at some other isolated site. The relationship between the indices and the lifetimes can be found to be

$$\tau_s = n_c \tau_c / n_s = \tau_o / n_s$$

where $\tau_s, \tau_c, and \tau_o$ are the lifetime values for the ionic emission in the small particle, crystal, and vacuum cases, respectively.

2.3 Temperature Effects on the Fluorescence Lineshift, Intensity and Absorption

Emission spectra lines are characterized by a wavelength for which the intensity is largest. The emission spectra line value typically alters with changes in temperature and is referred as the lineshift. The associated spectral emission width at the half maximum line intensity is referred to as the emission line width. Lineshift and linewidth deviations as a function of temperature are generally diminutive and are not often used as the
correlator in fluorescence thermometry. Literature has presented this latter technique for cathode ray tube thermometry where they observed a shift to the blue of about 0.2 nm in going from -15 °C to 72 °C [63].

Generally it is observed that emission spectra lines of phosphors get weak, i.e. become less bright, as the temperature of the material is increased. There may be regions where the selected emission lines are no longer sensitive to temperature deviations. The opposite effect may take place where at a particular value, termed quenching temperature, the strength of the emission line intensity falls dramatically. The quenching temperature and temperature dependencies vary for each type of phosphor and for each of the emission lines within the spectrum of a given phosphor.

When a phosphor is excited by a pulsed source, the persistence of the resulting fluorescence can be observed providing the length of the excitation source is much shorter than the persistence time of the phosphor’s fluorescence. The fluorescence intensity usually decays exponentially according to the relation

\[ I = I_o e^{-t/\tau} \]

where \( I_o \) is the value of \( I(t) \) at \( t = 0 \), and \( \tau \) (lifetime or 1/decay rate) is the standard 1/e (\( \approx 37\% \)) folding time for the fluorescence. The decay time is often an extremely sensitive function of temperature and, therefore a determination of its value constitutes a very useful method for fluorescence decay thermometry. At high impurity dopant concentrations, double exponential and more complex decay behaviors may arise which are more strenuous to analyze.
To have a thorough technical acquaintance of the operation of the fiber optic temperature sensor presented in this work, it is necessary to examine the theories of multiphonon relaxation and phonon-assisted energy transfer in rare earth doped crystals. The absorption of thermal energy by a material causes vibrations in the lattice, which can be treated as discrete packets of energy called phonons. The vibrations of a crystal lattice have a certain impact on physical processes proceeding in the solid body. For example, the vibrational motion of atoms is the main contribution to the heat capacity of a solid and serves as the primary mechanism for heat conduction. The mobility of electrons in a crystal, and consequently, its heat conductivity is determined to a considerable extent by lattice vibrations. Phonons can interact with impurity ions of a given host lattice, causing phonon-assisted energy exchange between ions, or stimulating the relaxation of the excited ion to a lower level via non-radiative decay. The latter process is termed multiphonon relaxation, and phonon-assisted energy transfer has successfully been observed for various combinations of donor and acceptor rare earth ions in yttrium oxide ($Y_2O_3$) at low temperatures.
3.1 Theory of Multiphonon Relaxation In Rare Earth Doped Crystals

It was early in spectroscopic studies of materials when the dilemma of multiphonon orbit-lattice relaxation of excited states of rare earth ions in crystals arose. These studies observed that fluorescence from the upper of two adjacent states can be significantly quenched if the energy separation between the two states is too small. For example, in LaCl$_3$ a rule of thumb has developed which states that a level which is 1000 cm$^{-1}$ or less above the next level will not, in general, be sufficiently long lived to fluoresce [64]. This phenomenon was explained as being a result of energy being dissipated to the lattice non-radiatively as phonons. From this phenomenon and the low maximum phonon energies of the materials examined, it was apparent that the process was of a high order involving several phonons [65].

Experimentally, the dependence of fluorescence quenching on the transition energy gap was observed through excited state lifetime measurements [66,67]. The critical energy gap has been observed to be different in various crystal hosts. Experimental results and subsequent analysis on relaxation rates between various excited levels of rare earth ions in laser crystals have shown the process to depend exponentially on the energy gap between levels involved in the process [68]. A greater separation of the excited state and the immediate lower lying level will require a larger number of phonons to conserve energy, and relaxation via nonradiative decay is less probable. In addition to the critical energy gap dependence, a dependency on temperature has been found to increase transition rates dramatically at elevated temperatures.
3.1.1 **Orbit-Lattice Interactions**

The modulation of the crystalline electric field by lattice vibrations instigates the interaction of an isolated rare earth ion with its dynamical crystalline environment. Expanding the crystal field Hamiltonian $H_{CF}$ in a Taylor series about the equilibrium ion position yields [68,69]

$$
H_{CF} = V_{CF} + \sum_i V_i Q_i + \frac{1}{2} \sum_{i,j} V_{i,j} Q_i Q_j + \ldots ,
$$

(3.1)

where $Q_i$ represents the $i$th normal mode coordinate and $V_{i,j}$ are partial derivatives of the static crystalline field $V_{CF}$ in the normal coordinate system.

$$
V_i = \frac{\partial V_{CF}}{\partial Q_i} \quad \& \quad V_{ij} = \frac{\partial^2 V_{CF}}{\partial Q_i \partial Q_j} ,
$$

(3.2)

Therefore a given term of the interaction Hamiltonian is a product of two terms, one of which operates on the atomic system and one on the lattice vibration system. The expansion in equation (3.1) is extremely complex for all but the simplest crystals.

The occurrence of processes involving the emission of many phonons can be accounted for by considering the first-order term in the expansion and carrying this out to high orders through perturbation theory. In time dependent perturbation theory, a process involving the transition from electronic state $|\Psi_a\rangle$ to electronic state $|\Psi_b\rangle$ with the emission of $p$ phonons can occur in diverse ways. When only the contributions from the two extreme terms are regarded and summing over all possible intermediate states and phonon modes, the probability for multiphonon relaxation between electronic states $|\Psi_a\rangle$ and $|\Psi_b\rangle$ involving $p$ phonons is given by
\[
W(p) = \frac{2\pi}{\hbar} \sum_{i,j,m_i \cdots m_{m_i}} \left| \langle n_i + 1|Q_i|n_i \rangle \right|^2 \cdots \left| \langle n_j + 1|Q_j|n_j \rangle \right|^2 \\
\times \frac{\left| \langle \Psi_{m_i} | V_{m_i} \Psi_{m_{m_i}} \rangle \right|^2 \cdots \left| \langle \Psi_{m_i} | V_j | \Psi_{a_j} \rangle \right|^2}{(E_{m_{m_i}} + \hbar \omega_i + \cdots + \hbar \omega_{j-i} - E_a)^2 \cdots (E_{m_i} + \hbar \omega_i - E_a)^2} \\
\times g(\omega_1) \cdots g(\omega_j) \delta(E_b + (\hbar \omega_1 + \cdots + \hbar \omega_j) - E_a) \\
+ \frac{2\pi}{\hbar} \sum_{i,j} \left( \frac{1}{n!} \right)^2 \left| \langle \Psi_{b_i} | V_{i-j} | \Psi_{a_j} \rangle \right|^2 \left| \langle n_i + 1|Q_i|n_i \rangle \right|^2 \cdots \left| \langle n_j + 1|Q_j|n_j \rangle \right|^2 \\
\times g(\omega_1) \cdots g(\omega_j) \delta(E_b + (\hbar \omega_1 + \cdots + \hbar \omega_j) - E_a)
\]

In equation (3.3) \( n_i \cdots n_j \) represent phonon mode occupation numbers, \( |\Psi_{m_i} \rangle \cdots |\Psi_{m_{m_i}} \rangle \) are intermediate virtual states, and \( g(\omega_1) \cdots g(\omega_j) \) are frequency densities of phonon states. The electronic levels are assumed to be infinitively narrow and energy conservation is guaranteed by the delta function. The summation is over all possible intermediate states and phonon modes.

Although the evaluation of equation (3.3) is possible in principle, in practice only order of magnitude estimates are feasible [69]. The computation of transition rates are not likely using equation (3.3) due to an n-fold convolution of the density of phonon states that would have to be performed. The greatest difficulty arises from a lack of detailed information regarding the frequency, polarization, and propagation properties of the vibrations which limits its use to order of magnitude calculations. In addition, there is not sufficient data pertaining to the associated strength of the ion-phonon coupling coefficients \( V_i, V_j \cdots \). However, these complexities lead to a simplified phenomenological approach. Due to the interaction of the large number of phonon
modes and intermediate states, it is assumed that these modes and levels will be statistically averaged out for high order processes. In the first approximation, it is expected that only the lowest order process dominates so only the $W(p)$ with the smallest $p$ contributes.

3.1.2 Energy Gap Dependence

The simple consequence of the convergence of terms of the perturbation expansion given in equation (3.3) is the dependence of the multiphonon transition rate on the energy gap. The ratio of the $p$th-order transition to the $(p-1)$th-order transition rate in a specified crystal is given by [68,69]

$$\varepsilon = \frac{W^{(p)}}{W^{(p-1)}} \ll 1,$$  \hspace{0.5cm} (3.4)

where $\varepsilon$ is a coupling constant characteristic of the host crystal which is necessarily small to ensure swift convergence of the expansion. The $p$th-order process approximately tracks the equation

$$W^{(p)} = Be^p,$$  \hspace{0.5cm} (3.5)

where $B$ represents some constant.

If the lowest-order process permitted dominates the decay, then the order is approximately determined by the energy gap according to the following expression:

$$p_i = \frac{\Delta E}{\hbar \omega_{\text{max}}} = \frac{\Delta E_{\text{MP}}}{E_p^i}.$$

(3.6)

38
where $\omega_{\text{max}}$ is the frequency cutoff of the phonon spectrum and $E_p$ is the phonon mode energy. Using equations (3.5) and (3.6), and disregarding any selection rules, the dependence of relaxation rate on energy gap is given by

$$W_{MP} = C e^{-\alpha \Delta E_{MP}},$$

where $C$ and $\alpha$ are constants which are characteristic of the particular crystal. Equation (3.7) is known as the energy gap law or exponential law due to the dependence of $W_{MP}$ on the energy gap $\Delta E_{MP}$ between electronic levels.

### 3.1.3 Temperature Dependence

A simple model for the temperature dependence of multiphonon relaxation is given by

$$W_{MP}(T) = W_{MP}(0) \left(1 - e^{\frac{E_p}{kT}}\right)^{-p_i},$$

where $W_{MP}(0)$ is the spontaneous transition rate at low temperatures given by equation (3.7) [i.e. $W_{MP}(T)=W_{MP}(0)$ at $T=0$ and the phonons are all in their ground state][69].

The total relaxation rate, sum of radiative and non-radiative rates, for ions in a excited host crystal lattice with coupling to one phonon mode is given by

$$W_{MP}(T) = A + C e^{-\alpha \Delta E} (1 - e^{\frac{E_p}{kT}})^{-p_i},$$

where $A$ is the radiative rate (assumed to be temperature independent). In a two phonon model, the total rate becomes

$$W_{MP}(T) = A + C_1 e^{-\alpha_1 \Delta E} (1 - e^{\frac{E_{p_1}}{kT}})^{-p_{i_1}} + C_2 e^{-\alpha_2 \Delta E} (1 - e^{\frac{E_{p_2}}{kT}})^{-p_{i_2}}.$$
Equation (3.10) is simply a modification of equation (3.9) containing the appropriate constants for the second phonon mode.

3.2 Theory of Phonon-Assisted Energy Transfer In Rare Earth Doped Crystals

Energy transfer processes are very vital in solid-state luminescent systems, because they may provide an enhancement or degradation of the luminescent emissions. This is usually achieved by the introduction in the host material of an ion of different type called acceptor or activator, in addition to the donor or sensitizer ion. The ion responsible for the desired emission is the acceptor ion. The donor ion provides additional spectral bands that absorb the pumping energy of the source in the system. The energy absorbed results in the excitation of the donor ion. In turn this excitation energy is transferred to the acceptor providing another means of non-radiative decay. This process leads to a greater probability for amplified decay rates. Of course, if the activator's decay is radiative, an enhancement of the emission may result; if it is non-radiative, quenching of the emission will be the consequence. The term phonon-assisted energy transfer generally means a non-resonant energy transfer process in which the mismatch of energy between the levels of energy donor and acceptor ions is compensated by the simultaneous emission or absorption of one or more phonons. This energy transfer process is governed by electron-phonon interaction as other vibronic processes are. The probabilities of phonon-assisted energy transfer as well as multiphonon relaxation are decreased approximately obeying exponential functions with the increase of energy gap. The parameters expressing the exponential dependence in these two processes are related
with each other. A dependency on temperature increases transition rates at elevated temperatures for this process in addition to the energy gap dependency.

3.2.1 *Energy Gap Dependence of Transfer Probability*

The probability of phonon-assisted energy transfer according to the Miyakawa-Dexter theory [70,71] is expressed by

$$ W_{PAT}(\Delta E) = W_{PAT}(0) \ e^{-\beta\Delta E_{PAT}} $$

where $\Delta E_{PAT}$ is the energy gap between the levels of donor and acceptor ions and $\beta$ is a parameter determined by the strength of the electron-phonon coupling as well as the nature of the phonon involved and is determined by the host crystal. Equation (3.11) has the same form as that for the energy gap dependence of the multiphonon relaxation rate given in equation (3.7).

The parameter $\alpha$ for multiphonon relaxation and $\beta$ in equation (3.11) are related to each other by

$$ \beta = \alpha - \gamma $$

and

$$ \gamma = \frac{1}{\hbar \omega} \ln \left( 1 + \frac{g_b}{g_a} \right) $$

where $g_a$ and $g_b$ are electron-lattice coupling constants for the acceptor and donor ions, respectively. The expression $\hbar \omega$ is the energy of the phonon mode which contributes dominantly to the process.
3.2.2 Temperature Dependence of Transfer Probability

Only spontaneous emission of phonons occurs at low temperatures. As temperature is increased, phonon-assisted energy transfer rate grows as a result of stimulated emission of phonons becoming operative. The temperature dependence of phonon-assisted energy transfer rate can be expressed as

\[ W_{PAT}(T) = W_{PAT}(0) \left(1 - e^{-\frac{E_p}{kT}}\right)^{-N}, \]

if it is assumed that the phonons involved in the energy transfer are of equal energy. The number of phonons \( N \) emitted in the processes is given by

\[ N = \frac{\Delta E_{PAT}}{E_p}, \]

where \( \Delta E_{PAT} \) is the difference between the transition energy of the donor and the transition energy of the acceptor, usually referred to as the energy gap. The parameter \( E_p \) is the energy of the relevant phonon mode in the host crystal.
CHAPTER 4

FABRICATION OF FIBER OPTIC FLUORESCENCE DECAY TEMPERATURE SENSORS

There has been interest on crystalline materials prepared in the fiber form for a sustained period of time. This is partially due to single crystal fibers possessing near ideal physical properties in crystallinity and in tensile strength. Earlier work was addressed mostly on metallic materials such as the successful pulling of single crystal metallic filaments directly from melt by Von Gompers in 1922 [72]. In the 1950’s work began to be centered on the magnetic and mechanical properties of metallic filaments [73] although the size and composition of these fibers could not be controlled with precision.

One method which allows the growth of crystalline fibers in a semi-controlled manner is the Steponav method in which the melts are drawn through shapers and crystallization is made to occur after passage through a die [74]. Another method that has enabled us to grow high quality single crystal fibers of a desired length and diameter with proper crystallographic orientation, composition and doping is the Laser Heated Pedestal Growth (LHPG) technique [75]. The LHPG method is classified under the non-conservative crystal growth process. In this process the solid is melted into the molten zone while crystallization is in progress.

Laser heating in the floating zone technique was used to grow single crystals of high melting point oxides, e.g., Y$_2$O$_3$, Al$_2$O$_3$, and Nd$_2$O$_3$ [76]. The floating zone technique has been applied in conjunction with a four-beam laser heating method to grow
fibers of high strength and light weight composites [77]. Single crystal fibers of Nd:YAG and Nd:Y$_2$O$_3$ were grown by Burrus and Stone [78] using a modified floating zone technique. The development of an axial-symmetric focusing system at Stanford University [79] for use with LHPG enabled for the first time uniform heating of the molten zone with a single laser beam.

4.1 *The Laser Heated Pedestal Growth (LHPG) Process*

LHPG and the related float zone growth technique are micro-variants of the Czochralski growth method. A number of heating sources have been used to produce the molten zone, with the most common method by far has being laser heating with single or multiple focused beams. A seed is inserted into the molten zone; as it is pulled out, surface tension of the molten materials forms a pedestal around the seed, hence the name pedestal growth. The melt is kept in place solely by surface tension, eliminating the need for crucibles and eliminating one high source of sample contamination. This type of container-less growth apparatus permits the synthesis of materials with extremely high melting points. Illustrations and schematic representations of the LHPG method for fiber growth showing various regions involved in the growth can be found in literature [80].

Conventional LGPG fiber pulling systems incorporate a stabilized CO$_2$ continuous wave (CW) laser typically with an output of between 15 – 75 W as a heating source. The usual focusing and turning optics can be found in literature [80]. The fiber pulling system has the capability to be enclosed in vacuum-tight chamber allowing growth in controlled atmospheres [81]. The source rods are usually cut out of polycrystalline ceramics produced by mixing host and activator materials, sintering and
hot pressing the mixture into flat disks. Crystalline feedstocks and fibers are typically used as source materials as well.

4.2 Advantages of the Laser Heated Pedestal Growth (LHPG) Technique

One of the most attractive features of the LHPG method is the rapidity with which fibers can be grown. With our pulling speeds fibers can be grown within a relatively short time. This allows for informational feedback for the rapid readjustment of stock compositions and growth conditions for optimized materials making this method a powerful tool in the synthesis and engineering of crystalline materials in general. Fiber configuration is ideal for experimentally conducting absorption, emission and other optical measurements.

The source rod length and the melt volume in LHPG applications are typically small. The cost of the chemical compounds required for the growth of single crystal fibers is relatively small as a consequence. This results in the possibility to grow fiber crystalline materials which would be prohibitively expensive to grow by traditional methods [82].

With the dependence on surface tension to maintain the integrity of the melt, the LHPG eliminates the need for crucibles or walls heated to high temperatures causing thermal gradients and stresses as is the case in crystal growth furnaces. Both crucibles and furnaces are well understood primary sources of unintentional contamination in normal crystal growth. The absences of these surfaces allow for the growth of very pure crystal materials that are practically stress free. The small volume of the growth area impedes in the introduction of external perturbations during the synthesis of the crystal
growth process. Impurity levels found in LHPG fibers are ordinarily solely determined by the purity of the starting materials of the source rods.

4.3 *The LHPG Station at the University of South Florida*

The LHPG station located at the University of South Florida has been in operation for nearly twenty years. The growth apparatus is composed of a stabilized 40 watt CO$_2$ laser manufactured by MPB Technology. The output of this laser is sent through a power attenuator and a beam expander before entering the growth chamber. Inside the growth chamber exists an optical system produced by Pneumo Precision Inc. consisting of a reflaxicon, a scraper mirror and a parabolic mirror. A detailed illustration of apparatus can be found in literature [80-82]. The optical system employed in this particular LHPG growth station enables the 10.6 $\mu$m radiation to focus axial-symmetrically on the molten zone. By lowering a seed crystal into the melt, crystal growth proceeds by simultaneous upward translation of the seed and source rods while maintaining a constant melt volume at the laser focus. The latter function is performed by a computer which controls the growth rate and the diameter reduction of the crystal. It is imperative that the melt volume be held constant to obtain uniform diameter fibers.

The transport systems for the upper and lower translators are identical. Brushless encoder servo motors equipped with the appropriate gear reduction ratios rotate a precision lead screw which in turn translates a hollow steel cylinder vertically. The cylinder holds a rod that has a removable tip assembly for a seed or feed source material to be secured. The growth chamber is made of heavy nickel-plated aluminum and is isolated from electric motors, mechanical stages and other extraneous objects which may
degrade the crystal growth process. This growth chamber features a contamination free environment for crystal growth which can be evacuated by a turbo molecular pump and back-filled with high purity gases to give an inert or reactive growth atmosphere.

4.4  Properties of Yttrium Aluminum Garnet (YAG)

Yttrium aluminum garnet (Y₃Al₅O₁₂), or YAG, is one of the most important optical materials with a wide range of applications such as laser host material, optical lens, and thermal barrier coating [83,84]. This is primarily attributed to its outstanding mechanical stability, low thermal expansion and conductivity, low acoustic losses, and excellent optical properties. YAG has a cubic garnet structure with space group $Ia3d$ or $O_h^{10}$ consisting of interconnected and slightly distorted octahedrons, tetrahedrons, and dodecahedrons with shared oxygen (O) atoms at the corner [85]. The Yttrium (Y) ion at the 24(c) position is dodecahedrally coordinated to eight O ions, which occupy the 96(h) sites. There are two aluminum (Al) sites, the octahedrally coordinated Al$_{oct}$ at the 16(a) site and the tetrahedrally coordinated Al$_{tet}$ at the 24(d) site. Different cation environments and the cubic structure are the basis of many of its electro-optical and electro-ceramic applications [83,84]. Because of its complex crystal structure, the electronic structure of YAG has only been studied recently [86,87].

YAG is a mechanically strong, thermally robust, and chemically resistant material. YAG is also a very valuable component in high temperature ceramic composites because of its well known resistance to creep [88-91]. Table 1 lists some of the important mechanical, thermal, optical and chemical attributes of YAG. The mechanical and chemical stability is comparable to sapphire crystal, but YAG is unique with non-
birefringence and available commercially with higher optical homogeneity and surface quality.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>4.5 g/cm³</td>
</tr>
<tr>
<td>Transmission Range</td>
<td>250 – 5000 nm</td>
</tr>
<tr>
<td>Melting Point</td>
<td>1970 °C</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>590 J/kg*°K</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>14 W/m°K</td>
</tr>
<tr>
<td>Thermal Expansion</td>
<td>6.9x10⁻⁶°K</td>
</tr>
<tr>
<td>Mohs Hardness</td>
<td>8.5</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.8197@1.0μm, 1.8121@1.4μm</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>a=12.004 Å</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>300 GPa</td>
</tr>
</tbody>
</table>

Table 4.1: Selected Properties of YAG.

4.5 Fabrication of the Single Crystal YAG Leads for Temperature Sensor

The single crystal YAG lead fiber served as the optical waveguide to transport the excitation radiation and fluorescence to and from the transducer tip, respectively. By lowering a YAG seed crystal oriented in the [111] direction into the molten zone, crystal growth proceeds by simultaneously upward translation of the seed and source rod while maintaining the constant melt volume at the laser focus as mentioned in section 4.3. All the lead fibers were grown first, measuring 450 μm in diameter and approximately 25 cm in length at a growth rate of 2.5 mm per minute. All the crystal growth runs were fabricated with 1 atmosphere (768 torr) of air in the growth chamber.

To prepare the lead fibers for optical testing, the two ends of each of the YAG lead fibers were mounted securely inside a short precision capillary tube with wax and then assembly was cut by a low speed diamond wheel saw to provide a semi-smooth surface normal to the fiber axis for polishing. Diamond lapping films were used
successively in finer grades to achieve a good optical surface finish to ensure optimal coupling of excitation source light into and out of the fibers. Transmission of each fiber was determined by measuring the ratio of the output power to the input power using a HeNe laser centered at 632.8 m with a power meter. Minimum transmissions of 70% of the original signal were measured for all the lead fibers used in this dissertation project.

4.6 Preparation and Fabrication of the Rare Earth Doped YAG Phosphor Tips

The substitution of the rare earth ions into the YAG lattice takes place in yttrium sites. The generic doping formula for all the transducer tips can be expressed by

$$A_xYb_3Y_{3-x-y}Al_{5}O_{12}$$

where different concentrations of Yb$^{3+}$ and a codopant (if used) rare earth ion represented by A are substituted in for yttrium. Table 2 shows a list of the ionic radii of various rare earth ions.

<table>
<thead>
<tr>
<th>Rare Earth Ion</th>
<th>Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>1.18</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>1.14</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>1.14</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>1.12</td>
</tr>
<tr>
<td>Pm$^{3+}$</td>
<td>1.10</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>1.09</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>1.07</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>1.04</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>1.03</td>
</tr>
<tr>
<td>Y$^{3+}$</td>
<td>1.02</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>1.02</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>1.00</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>0.99</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>0.98</td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 4.2: Ionic radii of rare earth ions [85].
earth ions which can be substituted into the yttrium sites of the garnet host. The steady
decrease in size of the ions with increasing atomic number illustrates the lanthanide
contraction. It can be seen from the table that Ho, Er, Tm and Lu can be substituted into
the YAG lattice relatively easily due to their ionic radii being less than or equal to that of
the yttrium ions. For larger ions such as Nd, only a limited amount can be introduced
into the crystal. At high doping levels significant lattice strain will result which will be
detrimental to crystal quality.

The starting materials for fabrication of all the transducer tips were $\text{Y}_2\text{O}_3$ and
$\text{Al}_2\text{O}_3$. Dopants in the form of $\text{Er}_2\text{O}_3$, $\text{Nd}_2\text{O}_3$, and $\text{Yb}_2\text{O}_3$ were added to the mix. For the
$\text{Yb}_3\text{Al}_5\text{O}_{12}$ base transducer tips, no $\text{Y}_2\text{O}_3$ was used since we substituted ytterbium ions in
for all the yttrium ion sites. All the oxide powders were bought from Alfa Aesar Inc.
having purities of 99.99% with respect to other rare earth constituents. The rare earth
oxides used to prepare the feed material for the transducer tips were baked at 1273 °C for
8 hours overnight in order to ensure its sesquioxide ($\text{RE}_2\text{O}_3$) composition. All of the
powders were baked in separate ceramic alumina dishes.

After the constituents were dried out to remove any moisture they were measured
out to 0.1 mg using an electronic balance. The materials were thoroughly mixed together
to ensure a uniform distribution of the elements. The mixed powder was then pressed
into a pellet using a 32 mm diameter die (Spex Corporation) mounted in a Specac 25 ton
uniaxial press. The amount of pressure needed to achieve adequate packing depends on
the amount of powder being pressed. Extreme pressures lead to cracking of the pellet in
two halves due to the flow of the powder from the center of the die towards its walls. We
found that a total pressure of about 20 tons was sufficient to achieve compaction with
minimum flaking and no cracking of our sample. The first step in the packing action for
our sample involves applying a pressure of approximately 5 tons to get rid of the
entrapped air in the die. After one hour the final pressure of 20 tons is applied to the
sample for 5 hours.

Once the sample has been pressed at a pressure of 20 tons for 5 hours it can be
removed from the die and is ready for the sintering process. Sintering is a vital process to
reduce the porosity in our sample and to aid in partially fusing the particles below their
melting. The sintering process is typically accomplished by heating the sample to a
temperature somewhere between ½ and ¾ of the melting point of the sample for a certain
period of time. During this process, the sample shrinks, particles join together, and much
of the void volume, which resulted from the initial misfit of the powder particles, is
eliminated. In the case of solid phase sintering, it occurs through the diffusion of the
particles in the volume of the material. The sintering temperature should be chosen based
on the lowest melting point of the constituents in the sample. All of our samples were
sintered for 8 hours at 1500 °C.

A typical feed preparation for growing our rare earth doped YAG transducer for a
phosphor with 2% Tb\(^{3+}\) and 10% Yb\(^{3+}\) is given here. The congruent melting formula for
YAG is:

\[ Y_3Al_5O_{12} \]

Since Tb\(^{3+}\) and Yb\(^{3+}\) ions will occupy yttrium sites, the congruent melting formula for
2%Tb,10%Yb\(\):YAG is:

\[ \text{Tb}_{0.06}\text{Yb}_{3}\text{Y}_{2.64}\text{Al}_5\text{O}_{12}. \]

The chemically balanced equation for this particular temperature sensor is:
\[
\frac{2.64}{2} (Y_2O_3) + \frac{0.06}{4} (Tb_4O_7) + \frac{0.3}{2} (Yb_2O_3) + \frac{5.0}{2} (Al_2O_3).
\]

Using the formula weights in mg of the respective oxides, we find that 298.1 mg of Y\(_2\)O\(_3\), 254.9 mg of Al\(_2\)O\(_3\), 59.1 mg of Yb\(_2\)O\(_3\), and 11.2 mg of Tb\(_4\)O\(_7\) will form slightly greater than 600 mg of the congruent mix which would be costly. The constituents were weighed out in ratios such that 1.5 grams of Y\(_2\)O\(_3\) was used per disc. This conveniently provided packed powder discs 1 mm in thickness which made feedstock cutting process less tedious when it was time to cut the samples into 1 mm x 1 mm strips.

The amount of laser power required for crystal growth is dependent on the melting point temperature of the garnet and the cross sectional size of the feed rod. The melting point of YAG is 1970 °C. It requires approximately 27 watts of CO\(_2\) laser power to melt a 1x1 mm square feed rod. Since the power requirement scales proportionately with the cross sectional area, we could not use feed rods larger than the 1x1 mm due to the lack of enough laser power.

Single crystal YAG fibers can be grown from crystalline feed at the rate of several mm/min with stellar crystal properties in contrast to ceramic or polycrystalline feeds. Rapid growth rates for polycrystalline and ceramic feeds are not feasible due to the entrance of air bubbles into molten zone being trapped in the grown crystal. Fast growth rates also incorporate major compositional variation along the growth axis. A growth rate of 0.1 – 0.2 mm/min was found to be appropriate for good crystal growth and quality.

Oriented seeds were used to initiate the growth of the doped and codoped transducer tips. Two growth generations were required to attain optimal optical quality from the packed powder. Therefore the feedstock was first grown into a cylindrical rod with a diameter of 600 μm. The transducer tip was then grown from this rod measuring.
1.5 – 5 mm in length and 450 μm in diameter directly onto the 24 cm YAG lead fiber resulting in a monolithic crystalline sensor measuring approximately 25.5 cm in length. Many papers have reported cited on the implementation of fiber optic temperature sensors based on fluorescence excited in a transducer tip [93-95]. The typical method of attachment was by either adhesive or mechanical means which limited their operation to about 1000 °C. With our monolithic probe assembly construction of the temperature sensor, the sensor should be operable up the high melting point of the YAG crystal provided there is a thermal source operable to that temperature.

All the temperature probes were annealed at roughly 1615 °C in a high temperature furnace with air inside to remove strain in the material and homogenize the dopant ions present in the crystal. We have found in our work with rare earth doped fiber optic temperature sensors that the annealing process is imperative in order to achieve reproducible and stable long term performance from our sensors. The sensors must be annealed at a temperature equal to or greater than the maximum temperature that the sensors will be used at for reproducibility. A ramp rate of 1 °C/min was used to heat and cool the fiber optic temperature sensor during annealing process to ensure the avoidance of thermal shock fracture. The furnace environment was kept extremely clean during the annealing process so that contaminating particles did not penetrate the surface of the fibers. Fiber transmissions are particularly sensitive to any surface modifications of this sort.
Homogenous incorporation and distribution of the rare earth dopant ions in the transducer tips for the fiber optic temperature probes is a necessity. When the dopants come from the melt phase into the crystal phase, its concentration has a change if the distribution coefficient $k_m$ is not equal to 1. If $k_m > 1$, the ion concentration in the crystal is larger than in the melt, and it is becoming lower from the top to the bottom of the crystal in the process of crystal growth, so a concentration gradient appears. Such gradients are known to be detrimental to performance in the field of laser physics. The distribution of rare earth ions such as Yb$^{3+}$ in YAG crystals can be calculated by the following formula:

$$k_m = \frac{c_{\text{top}}}{c_o},$$

where $c_{\text{top}}$ is the Yb$^{3+}$ (or other rare earth ion to be substituted for yttrium in YAG) concentration at the growth starting position in the crystal, and $c_o$ is the initial Yb$^{3+}$ concentration in the melt. Literature has concluded that the distribution coefficient of Yb$^{3+}$ in YAG crystals grown by the floating zone technique is $1.08 \pm 0.001$ [96]. The yttrium (YAG) and ytterbium (YbAG) garnets are isostructural with only a 1.5% difference in unit cell size [97] resulting in the easy substitution of Yb$^{3+}$ into the yttrium site in the dodecahedron for YAG. The distribution coefficient of other rare earth ions such as Nd$^{3+}$ and Tb$^{3+}$ might be slightly smaller in YAG than Yb$^{3+}$ ions. To ensure that ions with $k_m < 1$ values in the melt have attained a value approaching $c_o/k_m$, a length of the doped crystal measuring 20-30 mm will be grown first and pulled out of the molten zone. The cap on the feed now should have a dopant concentration of $c_o/k_m$, thus the phosphor tip on the probe will have a dopant concentration $c_o$ immediately. This allows
us to have transducer tips as short as possible resulting in the obviation of concentration gradients.
YTTERBIUM BASED FLUORESCENCE DECAY RATE FIBER OPTIC TEMPERATURE SENSOR SYSTEMS

Ytterbium doped materials have offered a wide range of applications over the last three decades from fiber lasers to amplifiers [98]. They have the ability to provide amplification over the very broad wavelength range from approximately 900 nm to 1200 nm which has generated substantial interest recently. Apart from their broad gain bandwidth, Yb doped fibers used in amplifiers can offer high output power and excellent power conversion efficiency [99]. There is a wide range of possible pump wavelengths, allowing a variety of pumping schemes, including the use of diode lasers or even high power Nd lasers.

Fibers doped with ytterbium have been investigated by some researchers for sensing applications. Yb based fluorescence was observed by Kimur et al. [101] at room temperature from Yb doped porous silicon layers prepared by an electrochemical method which was developed for Er doping of porous silicon layers. After rapid thermal annealing in a pure argon atmosphere at high temperatures above 900 °C, the samples showed a sharp fluorescence band at around 1.0 μm. Work by Maurice et al. [102] discussed an intensity based fiber optic sensor using specially developed and noncommercial Yb$^{3+}$ doped fiber of 40 μm diameter and 2000 ppm doping level. The device operated over a temperature range from room temperature to 600 °C, with an accuracy of 1 °C being reported. A particular advantage of this species is the facility to
use excitation sources which are cheap, high power, and readily coupled into a range of fibers, associated with a fluorescence emission spectrum in the near infrared which again is well suited to use with sensitive detectors.

5.1 Spectroscopic Properties of Yb:YAG

The spectroscopy of the Yb$^{3+}$ ion is relatively simple compared to that of other rare earth ions. For all optical wavelengths, only two groups of levels are relevant: the $^2F_{7/2}$ ground state manifold and the $^2F_{5/2}$ excited state manifold. Figure 5.1 illustrates the relevant energy levels of ytterbium in YAG. Previous work has shown that absorption and emission of Yb$^{3+}$ in YAG occur at 940 nm and 1040 nm, respectively [103]. The rare earth ion Yb$^{3+}$ has a very broad absorption band across the infrared spectrum, resulting from the $^2F_{5/2}$-$^2F_{7/2}$ transition shown in Fig. 5.1. Decay from the excited state $^2F_{5/2}$ metastable level is predominantly radiative because nonradiative transitions, due to phonon coupling or energy transfer with other energy levels, are inhibited except at very high temperatures. The 940 nm absorption peak is essentially due to the transition from the top of the lowest energy sublevel of the $^2F_{7/2}$ manifold to the middle of the upper $^2F_{5/2}$ Stark manifold. Four absorption bands exist for Yb:YAG crystals between 850 nm and 1100 nm [103]. The main absorption band centered at 940 nm has an FWHM of about 22 nm. A wide FWHM means that the crystal can accommodate some thermal shift of the pump light wavelength. The other two absorption bands are centered at 913 nm and 968 nm, respectively. Peak shifts in the absorption spectra for increasing doping concentrations of Yb$^{3+}$ in YAG have been observed due to lattice deformation. Lattice deformation increases the splitting of electronic manifolds that cause these observations.
Figure 5.1: Relevant energy level diagram of ytterbium pertaining to the operation of fluorescence decay rate temperature sensing.
As mentioned earlier in section 4.6, the effective radius of Yb$^{3+}$ is smaller than Y$^{3+}$, which is replaced by Yb$^{3+}$, leading to these slight deformations.

Research by Paschotta et. al. has revealed the fact that the details of the absorption and emission spectra depend, to some extent, on the host composition for rare earth ions [100]. The measured fluorescence decay times of Yb$^{3+}$ are typically around 1.0 ms and also vary by about 30% for different materials in fiber form. For example, fibers with higher germanium content in the core (introduced to achieve a higher numerical aperture) tend to have shorter lifetimes while Yb$^{3+}$ in a pure silicate glass has a lifetime of approximately 1.5 ms. The emission spectra may vary to some extent with pump wavelength, indicating some inhomogeneous broadening, although the broadening is predominately homogeneous [101].

### 5.1.1 Experimental Details for Yb Doped YAG Sensors

The optical arrangement for the acquisition of the temperature dependent fluorescence lifetime measurements for the ytterbium doped YAG sensors is shown schematically in Fig. 5.2. For excitation of the ytterbium based temperature sensors a high power laser diode was used centered at 940 nm with a FWHM of approximately 4 nm which well matches ytterbium’s main absorption band exactly. The 50 μs laser beam pulses at a repetition rate of 10 Hz were first collimated by a 1.5 cm focal length lens and reflected off a dichroic filter (HR at 940 nm, HT at 1040 nm). The reflected excitation beam is then focused into a 1 m length fiber patch cable with a 1.5 cm focal length plano-convex lens. The opposite end of the fiber patch cable was fixed to a stainless steel SMA to SMA mating sleeve that was used to connect to the ytterbium doped temperature
Figure 5.2: Schematic of the optical layout for the fluorescence decay rate measurements.
probes. The induced ytterbium fluorescence and scattered laser light propagate back through the YAG lead and fiber patch cable. After exiting the patch cable the beams are collimated by the plano-convex lens and the scattered laser light is reflected by the dichroic filter. A Si detector was used to detect the fluorescence emission at 1040 nm from the ytterbium ions and was acquired by a digital averaging oscilloscope for analysis. A type B thermocouple consisting of a pair of Pt/Rh wires was placed in close proximity of the phosphor to monitor the ambient temperature in the tube furnace. A PC was connected to the thermocouple and digital oscilloscope in order to collect 12 hour fluorescence lifetime data from the sensors using a LabView program.

5.1.2 Experimental Results for the Yb Doped YAG Sensors

Ytterbium doped YAG phosphor temperature probes with varying concentrations of ytterbium (5 at. %, 10 at. %, 20 at. % and 50 at. %) were fabricated as described in the former sections 4.6 and 4.7. Figures 5.3 and 5.4 display the fluorescence decay curves recorded for the 5 at. % Yb$^{3+}$:YAG phosphor sensor after $\lambda = 940$ nm pumping at 300 K and 1714 K, respectively. Figures 5.5 and 5.6 present semilog plots of the fluorescence decay curves for the former graphs, respectively. It is clearly discerned in these figures that the fluorescence decay for this sensor consists of only one exponential component by the successfully fitted linear lines in the figures 5.5 and 5.6. The fluorescence decay rate was determined to be 990 /s ($\tau = 1.01$ ms) at 300 K and 26,977 /s ($\tau = 37.1$ $\mu$s) at 1714 K. Fig. 5.8 exhibits the average fluorescence decay rate versus temperature for the 5 at. % Yb:YAG sensor (squares) from room temperature to 1714 K. Each fluorescence decay rate data point up to 1042 K in Fig. 5.8 is the average of four separate
measurements consisting of 256 decay traces. The time interval between adjacent
consecutive measurements was on the order of 30 seconds. Beginning at 1149 K,
fluorescence decay rate stability tests were performed for the 5 at. % Yb:YAG (squares)
sensor over a 12 hour period for every other data point represented in Fig. 5.8. The acute
break and abrupt proliferation in the fluorescence decay rates beginning at approximately
1500 K is attributed to the stimulated emission of phonons by thermally populated
phonon modes. Fig. 5.7 presents an exploded view of the fluorescence decay rates at
lower temperatures. The observed initial decrease in the fluorescence decay rates are due
to changes in thermal population distributions of the Stark levels of the $^2F_{5/2}$ manifold of
Yb$^{3+}$. This inhibits this sensor from being a candidate for temperature sensing
applications in regions below approximately 600 K due to the nonmonotonic nature of
the fluorescence lifetime making the determination of the decay time ambiguous.

As a comparison for the sensor just presented with the phosphor grown from
packed powder, a second 5 at. % Yb:YAG sensor was fabricated using a single crystal
feedstock purchased from Scientific Materials Inc. Fig. 5.8 shows the decay rate from
the probe grown from the single crystalline feed (hollow circles) and packed powder
feedstock (solid squares). Good agreement is reflected in the figure allowing for the
continued use of the packed powder feedstocks for fabricating the phosphors opposed to
purchasing the costly single crystalline sources.

It is clearly important in any practical application that a stable and reproducible
fluorescence response is seen for fiber-optic based temperature sensors. Figures 5.9-5.15
represent the results from 12 hour stability tests performed in the effort to determine if
any significant changes are apparent in the fluorescence characteristics when the 5 at. %
Figure 5.3: Temporal evolution of 1040 nm fluorescence of Yb$^{3+}$ ions ($^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$) at 300 K after pulsed excitation of the Yb$^{3+}$ ions at 940 nm.
Figure 5.4: Temporal evolution of 1040 nm fluorescence of Yb$^{3+}$ ions ($^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$) at 1,714 K after pulsed excitation of the Yb$^{3+}$ ions at 940 nm.
Figure 5.5: Temporal evolution (in semi-logarithmic scale) of 1040 nm fluorescence of Yb$^{3+}$ ions ($^2F_{5/2} \rightarrow ^2F_{7/2}$) at 300 K after pulsed excitation of the Yb$^{3+}$ ions at 940 nm.
Figure 5.6: Temporal evolution (in semi-logarithmic scale) of 1040 nm fluorescence of Yb³⁺ ions \( ^{2}F_{5/2} \rightarrow ^{2}F_{7/2} \) at 1,714 K after pulsed excitation of the Yb³⁺ ions at 940 nm.
Figure 5.7: Low temperature expanded view of the experimental data on fluorescence decay rate versus temperature for the 5%Yb:YAG sensor. The squares represent data taken on two separate occasions, two trials per occurrence, and the error bars represent the standard deviation of the four relaxation rate measurements.
Figure 5.8: Experimental data on fluorescence decay rate versus temperature for the 5%Yb:YAG sensor. The squares represent data taken on two separate occasions, two trials per occurrence, and the error bars represent the standard deviation of the four relaxation rates measurements. Open circles represent excursion taken using single crystal 5%Yb:YAG sensor for initial feedstock.
Figure 5.9: 12 hour fluorescence decay rate data for 5%Yb:YAG phosphor at 1,149 K +/- 1.3 K.
Figure 5.10: 12 hour fluorescence decay rate data for 5%Yb:YAG phosphor at 1,248 K +/- 0.68 K.

Average = 1,274/s
Standard Deviation = +/- 6.1/s
Figure 5.11: 12 hour fluorescence decay rate data for 5\%Yb:YAG phosphor at 1,344 K +/- 0.70 K.
Figure 5.12: 12 hour fluorescence decay rate data for 5%Yb:YAG phosphor at 1,439 K +/- 0.84 K.
Figure 5.13: 12 hour fluorescence decay rate data for 5%Yb:YAG phosphor at 1,530 K +/- 0.46 K.
Figure 5.14: 12 hour fluorescence decay rate data for 5\%Yb:YAG phosphor at 1,622 K +/- 1.4 K.
Figure 5.15: 12 hour fluorescence decay rate data for 5\%Yb:YAG phosphor at 1,714 K +/- 0.6 K.
Yb:YAG was exposed to elevated temperatures. It can clearly be seen that the standard deviations increased from the Figs. 5.9-5.15 as temperature was increased. This is attributed to the higher internal loss in the lead fiber at elevated temperatures. The experimental data reveals that one can determine the fluorescence decay rate to better than 0.08 % at the lowest temperature of 1149 K examined and to within 0.9 % at the highest temperature of 1714 K inspected. This increase is due to the reduction in the signal to noise ratio.

The relative sensitivity of the all crystalline fiber-optic temperature sensor probes used in this work can be given by

\[
S = \frac{1}{W(T)} \frac{\Delta W}{\Delta T}
\]

where \( W(T) \) is the fluorescence decay rate and \( \Delta W \) and \( \Delta T \) are respectively increments of the decay rate and temperature. Fig. 5.16 displays a semi-log plot of the 5 at. % Yb:YAG temperature sensor’s relative sensitivity for temperatures greater than 1100 K. The sensitivity has two linear regions, one being where the sensitivity progresses to a maximum value at a temperature of 1484 K and another region where it is declining from thereafter, with slopes of \( 0.0040 /K^2 \) (y-intercept of 3.44 /K) and \( -0.0035 /K^2 \) (y-intercept of -38.07 /K) respectively. A temperature measurement accuracy of approximately 1 K is obtainable with the lifetime measurement being determined to within 1.1 % at 1484 K.

Figures 5.17–5.19 exhibit an expanded view of the decay rates at lower temperatures for the 10 at. % Yb:YAG, 20 at. % Yb:YAG and 50 at. % Yb:YAG, respectively. Thermal redistribution of populated states among the Stark levels of the \(^2\)F\(_{5/2}\) manifold of Yb\(^{3+}\) again is responsible for the initial decline in the fluorescence decay rates in these figures similar to the results shown for the 5 at. % phosphor sensor.
The nonmonotonic regions in the decay rates for Figs. 5.17-5.19 at the low temperature end is suppressed to smaller domains with the incorporation of higher doping concentrations of the Yb$^{3+}$ ions in the host lattice. Figure 5.20 depicts changes in the multiphonon relaxation behavior by the advancement of the response to lower temperatures with increasing Yb$^{3+}$ dopant concentration due to alterations in the phosphors crystalline environment and phonon distribution. Increased dopant concentrations also result in a smaller interaction radius between luminescent sites and impurities or defects which are capable of extinguishing the excitation energy. Although the 5 at. % Yb:YAG phosphor had smallest nonmonotonic region for the varying Yb$^{3+}$ dopant concentrations, close examination of the phosphor portion of the sensor revealed poorer visual crystal quality than the other samples which may have contributed to this finding.

For comparison, Fig. 5.21 presents the results illustrating the relative sensitivity for the 10 at. %, 20 at. %, and 50 at. % Yb:YAG phosphors which are represented by the dotted, dash-dotted, and solid lines respectively. This figure clearly demonstrates that one can increase the relative sensitivity values at lower temperatures via the increase of Yb$^{3+}$ dopant ions into the host lattice of YAG. Although the relative sensitivity values decrease at the high temperature end earlier with greater dopant concentrations, it will be offset with better signal to noise ratios in concerns pertaining to temperature measurement accuracy. Stability data for these sensors are presented in Appendix.

An ytterbium aluminum garnet (YbAG) crystal was purchased from Scientific Materials Inc. to fabricate a YbAG phosphor sensor for analysis. The YbAG phosphor sensor was calibrated in the temperature region 298 K to 1373 K. The results illustrating
Figure 5.16: Relative sensitivity versus temperature (in semi-logarithmic scale) for 5%Yb:YAG sensor.
Figure 5.17: Low temperature expanded view of the experimental data on fluorescence decay rate versus temperature for the 10%Yb:YAG sensor. The circles represent data taken on two separate occasions, two trials per occurrence, and the error bars represent the standard deviation of the four relaxation rate measurements.
Figure 5.18: Low temperature expanded view of the experimental data on fluorescence decay rate versus temperature for the 20\%Yb:YAG sensor. The triangles represent data taken on two separate occasions, two trials per occurrence, and the error bars represent the standard deviation of the four relaxation rate measurements.
Figure 5.19: Low temperature expanded view of the experimental data on fluorescence decay rate versus temperature for the 50%Yb:YAG sensor. The inverted triangles represent data taken on two separate occasions, two trials per occurrence and the error bars represent the standard deviation of the four relaxation rate measurements.
Figure 5.20: Experimental data on fluorescence decay rate versus temperature for the 10%Yb:YAG (circles), 20%Yb:YAG (triangles), and 50%Yb:YAG (inverted triangles) sensors. Each data set represents data taken on two separate occasions, two trials per occurrence, and the error bars represent the standard deviation of the four relaxation rate measurements.
Figure 5.21: Relative sensitivities versus temperature for 10% Yb:YAG (dotted line), 20% Yb:YAG (dot-dash line), and 50% Yb:YAG (solid line) sensors.
Figure 5.22: Experimental data on fluorescence decay rate versus temperature for the YbAG sensor.
the fluorescence decay rate as a function of temperature are shown in Fig. 5.22. It can be seen that the fluorescence lifetime increases monotonically with the increase of temperature for temperatures exceeding approximately 675 K. For the first 200 K multiple data points where taken in order to obtain a good calibration curve for the low temperature region in order to deploy this sensor in the thermally compensated mode which will be presented in a later section.

The temperature dependence of the multiphonon transition rate from $^2F_{5/2}$ to $^2F_{7/2}$ in YbAG was inspected and is shown in Fig. 5.23. The observed reduction in the experimental data (open circles) initially is due to thermal redistribution of populated states similar to the formerly presented fluorescence versus temperature plots for the various Yb$^{3+}$ concentrations in YAG. The sharp break and increase in the multiphonon transition rate at higher temperatures is attributed to the stimulated emission of thermally populated phonon modes. The theoretical fit (black curve) corresponds to the emission of 12 phonons of energy 800 cm$^{-1}$ to bridge the approximately 9,600 cm$^{-1}$ energy gap of Yb$^{3+}$. The temperature dependent transition rate is given by

$$W_{MP}(T) = A + Ce^{-\frac{E_p}{kT}}(1 - e^{-\frac{E_p}{kT}})^{-12}.$$  

The fit with the experimental data for temperatures greater than 600 K to the pure 12 phonon decay is satisfactory. The decay involves the second highest reported optical phonon mode affiliated with YbAG [104]. When the highest optical mode and lower energetic modes were inspected, the fit got progressively worse with the experimental
data. The 800 cm\(^{-1}\) mode makes the dominant contribution to multiphonon relaxation and conserves energy in the lowest order process than the lower energetic modes.

The YbAG phosphor fiber optic temperature sensor was used in the effort to demonstrate the phenomenon of radiation trapping on the measured fluorescence lifetime of the phosphor. The room temperature fluorescence lifetime of the YbAG phosphor in ambient air was found to be 290.9 \(\mu\)s (3,436.8 /s). When the YbAG phosphor tip was immersed in distilled water the fluorescence lifetime was determined to be 281.4 \(\mu\)s (3,552.5 /s), corresponding to a 3.35 % reduction in the excited state lifetime compared to results obtained for air. This finding is attributed to radiation trapping in which emitted photons by the fluorescent Yb\(^{3+}\) centers are subsequently absorbed by centers in the distilled water. When the YbAG phosphor is immersed in the distilled water (\(n = 1.33\)), there is a smaller difference between the index of refraction with the phosphor (\(n = 1.82\)) compared to when the phosphor is surrounded by air (\(n = 1.00\)), promoting the fluorescent emission to escape easier. When the phosphor is surrounded by media with indices closer to its internal index of refraction (i.e. index-matched), the likelihood of excessive reabsorption and reemission processes are reduced considerably due a smaller critical angle for total internal reflections in the phosphor. The effects of repeated radiative energy transfer has been reported in literature for the excited state lifetimes of Yb:YAG and Er:YLF samples where reductions up to 25% were observed [109,110].

Our findings suggest that detailed information must be obtained in reference to a media’s index of refraction to make proper corrections in order to acquire accurate temperature measurements using phosphor based fiber optic sensors.
Figure 5.23: The multiphonon transition rate from the $^{2}F_{5/2}$ manifold of Yb$^{3+}$ in YbAG is shown as a function of temperature. The solid squares represent the theoretical curve corresponding to the stimulated emission of 12 phonons of energy 800 cm$^{-1}$ whose sum is approximately 9600 cm$^{-1}$. The circles represent the experimental data.
5.2 Spectroscopic Properties of Nd,Yb:YAG

As indicated previously in section 6.1.2, the 10%Yb:YAG sensor does not have any significant response until above 1,550 K. We were only marginally successful in extending its response to lower temperatures by codoping the 10%Yb:YAG sensing probes with Tb$^{3+}$ as reported in literature [54]. However, the studies of the effect of Tb$^{3+}$ on Yb:YAG fluorescence decay did lead to important new insights about phonon assisted energy transfer at very high temperatures. Building on this new found knowledge, we investigated the potential of Nd$^{3+}$ in extending the low temperature response of the temperature probes for the Yb:YAG sensors.

The relevant energy levels for the Yb-Nd system are shown in figure 5.24. For simplicity the Stark components within each level have been suppressed. The transition energy indicated for Yb$^{3+}$ is, as before, calculated from the middle of the upper manifold to the top of the bottom manifold. For Nd$^{3+}$, the Stark components are located at 0 cm$^{-1}$, 132 cm$^{-1}$, 200 cm$^{-1}$, 311 cm$^{-1}$, and 852 cm$^{-1}$ [105]. Because the highest state lies well above the rest, it can be disregarded. Therefore, the energy shown corresponds to that from the middle of the lower 4 states in the ground manifold to the top of the $^4I_{15/2}$ manifold.

5.2.1 Experimental Results for the Nd,Yb:YAG Sensors

In the effort to enhance the response of our Yb:YAG based FDR temperature sensor, we introduced Nd$^{3+}$ as the acceptor ion for energy transfer. The temperature dependence of the fluorescence decay rate for the phosphor containing 2 at. % Nd and 20 at. % Yb. are shown in Fig. 5.25. Fig. 5.26 presents an expanded scale at the low
Figure 5.24: Energy levels in ytterbium and neodymium relevant to the operation of Nd,Yb:YAG sensors.
temperature end for magnified inspection. Significant response is found for the phosphor at low temperatures (Fig. 5.26) extending further into the low temperature region by 600 K in comparison with the Tb,Yb:YAG sensor investigated in earlier work [1,30,37]. The dip prohibits the use of the Nd,Yb:YAG sensor below 520 K. The creation of the nonradiative pathway via energy transfer by the addition of the neodymium ions extends the response into the low temperature region by nearly 100 K, 600 K, 450 K, 150 K, and 175 K in comparison to the varying 5, 10, 20, 50, and 100 at. % Yb$^{3+}$:YAG phosphors presented in the previous section, respectively.

The sensitivity of the 2 at. %Nd, 20 at. %Yb:YAG sensor is shown in Fig. 5.27. The fluorescence lifetime for the 20 at. %Yb:YAG phosphor could be determined to within .03 % and 1 % at approximately 500 K and 1690 K, respectively. It is not unreasonable to expect the same accuracy in the determination of the fluorescence lifetime for the 2 at. %Nd, 20 at. %Yb:YAG phosphor. This would correspond to a sensitivity of 1.2 K at 500 K and 1.1 K at 1690 K.

The 2%Nd,20%Yb:YAG sensor was sacrificed to examine the dopant distribution along the growth axis. A multiline argon laser was used as the excitation source for the Nd$^{3+}$ ions at 514 nm which was modulated by using a variable frequency chopper (See Fig. 5.28). A prism made with 60 ° angles was used in the effort to disperse the multiline emission output of the argon ion laser. The dispersing properties of the material from which the prism is made allows for the spatial separation of different emission wavelengths of the argon laser. After blocking the unwanted laser emission lines, the 514 nm excitation light was modulated with a chopper and focused down onto the codoped fiber which was secured to a translation stage. A longpass filter (LP 1,000) was placed in
Figure 5.25: Experimental data on fluorescence decay rate versus temperature for the 2 %Nd,20%Yb:YAG sensor. The stars represent data taken on two separate occasions, two trials per occurrence, and the error bars represent the standard deviation of the four relaxation rate measurements.
Figure 5.26: Low temperature expanded view of the experimental data on fluorescence decay rate versus temperature for the 2%Nd,20%Yb:YAG sensor. The stars represent data taken on two separate occasions, two trials per occurrence, and the error bars represent the standard deviation of the four relaxation rate measurements.
Figure 5.27: Relative sensitivity versus temperature for 2%Nd,20%Yb:YAG sensor.
the path of the Nd emission to block any scattered light from reaching the detector and permit the 1.06 μm emission to pass. When a second longpass filter (LP 665) was placed in front of the detector along with the LP 1,000, our Nd emission signal was not altered. This verified that the use of just the LP 1,000 filter sufficed in blocking out all of the scattered laser light. For verification that we were receiving a real signal, the fiber was replaced with microslide in which no signal was apparent.

The crystal was polished to expose a flat crystal surface for analysis. The 2%Nd,20%Yb:YAG crystal analyzed was about 15 mm long and the entire length was analyzed. Fig. 5.29 shows the plot of the voltage (which represents the distribution of Nd dopant concentration) along the growth axis of the crystal. We would presume a uniform signal along the growth axis of the crystal providing the following conditions: 1.) the atomic weight fraction $C_A$ of the element of interest (Nd) is uniform, 2.) the excitation beam is always kept normal to the crystal’s surface, and 3.) the volume of the crystal from which the emission is generated is constant. Making certain that conditions 2 and 3 are met, any variations in the emission signal would denote a variation in $C_A$. The concentration of Nd in the crystal is controlled by the segregation coefficient of the ion in the crystal matrix. The first and the last data points were taken at positions close to the starting and ending points of the growth run, therefore they might have been affected by the unstable thermodynamics of the molten zone. As it is seen in Fig. 5.29, the Nd dopant concentration in the crystal approaches a constant value fairly slowly. Nd concentration in this crystal increased from a very low value near the junction with the lead YAG fiber to a final plateau concentration over a length of approximately 10 mm. This gradient is attributed to the relatively small distribution coefficient for the
incorporation of Nd into YAG, which results in the segregation of Nd ions in the grown crystal and the melt. This data implies that a length of at least 10-15 mm should be grown first to attain the desired feed concentration of 2 % Nd uniformly along the growth axis. This will ensure the concentration of Nd in the melt has attained a value approaching $c_0/k_m$. Once the Nd concentration has plateaued, we will be able to use the remaining feed to fabricate the fiber optic temperature probes. Since the cap on the feed now has a Nd concentration of $c_0/k_m$, the phosphor tip on the temperature probe will have a Nd concentration of $c_0$ immediately. The former described process was implemented on all the phosphor tips in this work.
Figure 5.28: Experimental setup for side fluorescence measurements for the 2%Nd,20%Yb:YAG sensor.
Figure 5.29: Experimental side fluorescence measurements for the 2%Nd,20%Yb:YAG sensor.
5.3 Spectroscopic Properties of Er, Yb:YAG and Er:YbAG

The experimental results from the Nd, Yb:YAG probe gave impetus to further investigate improvement at the low temperature end. Erbium (Er$^{3+}$) was chosen to be the candidate as the acceptor ion for energy transfer next. An interesting feature of Er, Yb:YAG system is the fact that the Yb $^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$ transition is resonant with the Er $^{4}I_{15/2} \rightarrow ^{4}I_{11/2}$ transition as shown in Fig. 5.30. The energy transfer process which occurs between these two ions is consequently also of a resonant nature. Due to the close energy match characteristic of the two levels $^{2}F_{5/2}$ (Yb) and $^{4}I_{11/2}$ (Er), the two levels should always be in thermal equilibrium and behave as a single manifold kinetically. The $\lambda = 940$ nm excitation energy, after being absorbed by the ytterbium ions, is transferred to the erbium ion level by a resonant nonradiative energy transfer process followed by fast nonradiative energy relaxation to the erbium level $^{4}I_{13/2}$. The efficiency of this ytterbium-erbium system is determined by the extent of overlap between Yb$^{3+}$ emission spectrum and Er$^{3+}$ absorption spectrum. It is also imperative that the transfer rate from ytterbium to erbium ions to be faster than ytterbium’s fluorescence decay rate.

5.3.1 Experimental Results for the Er, Yb:YAG Sensors

A 2%Er, 20%Yb:YAG temperature probe was fabricated for investigation. Fig. 5.31 displays the fluorescence decay rate versus temperature for this particular probe from 300 K to 1,071 K temperatures. From these graph it is distinctly shown that improvements in the response at the low temperature end have been made by the monotonic behavior of the experimental data in this region. Although we have made tremendous progress at achieving stronger response at the low temperature range, an abrupt reduction in the decay rate at temperatures greater than approximately 1070 K was
Figure 5.30: Energy levels in erbium and ytterbium relevant to the operation of Er,Yb:YAG sensors.
Figure 5.31: Experimental data on fluorescence decay rate versus temperature for the 2%Er,20%Yb:YAG sensor. The triangles represent data taken on two separate occasions, two trials per occurrence, and the error bars represent the standard deviation of the four relaxation rate measurements.
detected. This observation is credited to the excited ions decay process being in energy migration limited regime for the dopant concentrations examined. At elevated temperatures there may be a significant reduction in the extent of spectral overlap of the emission spectrum of $\text{Yb}^{3+}$ with the absorption spectrum of the $\text{Er}^{3+}$ due to the thermal shifts in their respective spectra. The number of excited $\text{Yb}^{3+}$ donors within the critical interaction range of acceptors may also be too small leading to the decay process being energy migration limited. This results in a time duration which is too long for $\text{Yb}^{3+}$ to exchange energy with another $\text{Yb}^{3+}$ ion within the vicinity of an $\text{Er}^{3+}$ acceptor ion. Fig. 5.32 illustrates the $\text{Yb}^{3+}$ fluorescence in a semilogarithmic plot for the 2%Er, 20%Yb:YAG probe at 300 K and 1145 K following pulsed excitation. Take note to the initial deviation from a simple exponential dependence for the plots at both temperatures. The initial nonexponential portion of the decay is attributed to scattered pump light leaking through the filter and relaxation by direct $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ energy transfer. At lower $\text{Er}^{3+}$ concentrations a smaller fraction of the excited $\text{Yb}^{3+}$ ions would be within the effective interaction sphere of $\text{Er}^{3+}$ energy sinks. This would lead to a smaller contribution of the direct relaxation process to the over-all decay and the nonexponential portion of the decays in Fig. 5.32 would effectively become smaller. However, lower codopant concentrations will also lead to a less pronounced variation of the fluorescence decay rate as a function of temperature which contradicts our objective to broaden the response range of the sensor. The final portions of both plots are exponential. Literature has reported the same initial nonexponential behavior for $\text{Cr}^{3+}$ doped Eu(PO$_3$)$_3$ in which the nonlinearity portion increases with $\text{Cr}^{3+}$ content [106]. Notice that the 1145 K plot has a much shallower slope than the 300 K plot. The slopes, which represent the decay
Figure 5.32: Temporal evolution (in semi-logarithmic scale) of 1040 nm fluorescence of Yb$^{3+}$ ions ($^2F_{5/2} \rightarrow ^2F_{7/2}$) at 300 K and 1,145 K after pulsed excitation of the Yb$^{3+}$ ions at 940 nm for the 2%Er,20%Yb:YAG sensor.
rate, should increase with increasing temperature when decay system is in the superfast migration regime. This is apparently not the case for the 1145 K plot due to the decay process being energy migration limited. The super fast migration regime is desired for simple interpretation of the data for temperature sensing applications.

In the effort to keep the fluorescence decay process in the superfast migration regime we decided to replace all of the yttrium ions with \(^{3+}\)Yb to form the host \(\text{Yb}_3\text{Al}_5\text{O}_{12}\) while still using \(^{3+}\)Er as the acceptor candidate of choice. Literature has reported that YbAG and YAG are isostructural with less than 1.5 % difference in unit cell size from lattice parameter data [107]. Recent literature has reported that the absorption coefficient of YbAG is 90.8 cm\(^{-1}\) at 940 nm [108]. This makes it very reasonable to expect essentially complete absorption of the pump radiation at this wavelength in a heavily doped Er:Yb\(_3\text{Al}_5\text{O}_{12}\) probe.

The temperature dependence of the fluorescence decay rate for probes containing 5%Er:YbAG (circles) and 10%Er:YbAG (triangles) are shown in Fig. 5.33. The room temperature lifetime for the 5%Er:YbAG sensor was found to be 0.31 ms which is reasonable considering reports from literature citing the lifetime of YbAG to be 0.27 ms [108]. One notices from the exploded low temperature graph given in Fig. 5.34 the recurrence of the dip as seen for other probes makes the 5%Er:YbAG sensor impractical for operation from room temperature to approximately 450 K. Due to the same feature in the fluorescence decay rate for the 10%Er:YbAG probe, this sensor is for deployment from room temperature to around 600 K. It can also clearly depicted for Figs. 5.33 and 5.34 that the fluorescence decay rate for the 5%Er:YbAG (circles) and 10%Er:YbAG (triangles) are comparable at temperatures greater than 900 K. This finding attests that
the additional Er$^{3+}$ concentration had no dramatic effect on the fluorescence decay rate for the concentrations investigated.
Figure 5.33: Experimental data on fluorescence decay rate versus temperature for the 5%ErYbAG (circles) and 10%ErYbAG (triangles) sensors. Each data set represents data taken on two separate occasions, two trials per occurrence, and the error bars represent the standard deviation of the four relaxation rate measurements.
Figure 5.34: Low temperature expanded view of the experimental data on fluorescence decay rate versus temperature for the 5%ErYbAG (circles) and 10%ErYbAG (triangles) sensors. Each data set represents data taken on two separate occasions, two trials per occurrence, and the error bars represent the standard deviation of the four relaxation rate measurements.
CHAPTER 6

THERMALLY COMPENSATED FLUORESCENCE DECAY RATE TEMPERATURE SENSOR

The material science and semiconductor manufacturing industries require improved accuracy in measuring the temperature of silicon wafers during processing because accurate temperature measurements are critical to product quality and device performance. In particular, there has been a long term established need for the enhancement in the accuracy of surface temperature measurements, with emphasis in the area of rapid thermal processing (RTP) of semiconductors and applications requiring temperature measurements where heating is accomplished via microwave radiation.

In order to measure the surface temperature of a heated object, the sensor must achieve adequate thermal contact with the sample of interest. Once the sensor has made contact, heat will flow from the object to the sensor, raising the temperature of the sensor in the process. Eventually thermal equilibrium will be reached by the sample and sensor. The final equilibrium temperature of the sensor will rely on a number of factors such as (1) the degree of thermal isolation of the sensor and the sample from the surrounding environment; (2) the surface area, quality and pressure of the thermal contact, and; (3) the thermal mass of the sensor relative to the sample.

Typical practices in surface temperature measurements involve the thermistor, thermocouple, or RTD to be secured to the sample via adhesives or epoxies. This technique provides secure attachment and a thermally insulating barrier over the sensor in
order to measure the sample temperature at the location of interest, but is not an option for, e.g., monitoring the temperature of a wafer being processed. In addition, removal of sensor may be tedious and cause damage to the sample of interest. If the sensor has poor contact or a large thermal mass relative to the sample, the measured equilibrium temperature will be below that of the true surface temperature prior to contact. Samples which are feeble conductors of heat may result in long equilibrium times due to the slow rate of heat flow to the location where heat is drawn by the sensor.

The most frequent challenge with surface temperature measurements with electrical sensors involves the sensor leads conducting heat away from the sample due to their being good thermal conductors, resulting in erroneous readings. In vacuum applications the above challenges tend to magnify since conduction by air is eliminated. In electrically hostile environments involving strong radio frequency (RF) or microwave fields, RF plasma, and high voltage gradients, the electrical sensors experience alarming problems which inhibit accurate surface temperature measurements.

In the infrared radiometry approach, uncertainties about the emissivity of the surface of interest leads to liberal errors. Many finished samples contain a variety of materials which are optically not resolvable from one another so the average observed emissivity is typically unknown. Furthermore, complications arise from some of the observed infrared energy being transmitted through semiconductor materials from a source somewhere behind the surface material of interest. Finally, field of view complications are typically associated with this technique making it an undesirable means of measuring surface temperatures.
The thermally compensated FDR temperature sensor technique is an entirely new approach. With the use of a second laser operated in the continuous wave (CW) mode as the internal heating mechanism, the phosphor tip will be heated up. First, the temperature of a phosphor probe at a series of CW laser power levels can be measured with its tip in close proximity to the point of interest on a surface. Another set of measurements is then made at the same series of launched CW power laser levels with the tip of the probe touching the surface of interest. Initial heating temperatures below that of the actual surface temperature will result in an increase of the tip’s temperature, and those higher would lead to a decrease. The smallest change in phosphor tip’s temperature will be experienced for initial temperatures that are closest to the actual surface temperature. When the temperature difference is plotted against temperature, where it crosses from negative to positive for the contacting and noncontacting conditions should then give the true surface temperature. This novel technique with the crossing principle should allow for the true surface temperature to be determined even without the true temperature being directly measured.

6.1 *Thermally Compensated Fluorescence Decay Rate Temperature Sensor Model*

A simple model for the thermal transport mechanisms of the thermally compensated fluorescence decay rate temperature sensor used in the experiment is provided in Fig. 6.1. The end of the 400 \( \mu \)m diameter sensor probe in which the pulse train excitation source and CW heating source will be coupled (end opposite of the phosphor tip) is mounted in a stainless steel SMA connector, which is assumed to be at room temperature \( T_0 \). It is further assumed that the phosphor will be cooled along the length of the growth axis of the lead fiber while simultaneously being heated via CW
Figure 6.1: Simplified model for the thermal transport mechanisms of the thermally compensated FDR YbAG sensor.
laser radiation. In addition, heat exchange between the phosphor with uniform
temperature $T$ and the surface of interest at temperature $T_s$ will be accomplished by
conduction through the surrounding gas medium. Thermal transport between the tip and
the sample of interest will be considered separately for the sidewall of the phosphor
transducer and its end. The conductive medium between the phosphor and the sample is
considered to be in the shape of a conical frustum with areas $\pi(a+d)^2$ for the top and $\pi a^2$
for the bottom, where $a$ is the radius of the probe and $d$ the distance between the
phosphor tip and the sample. The rate of heat transfer between the end of the phosphor
tip and the sample is given by $\pi \kappa a(1+a/d)(T_s-T)$, where $\kappa$ is the thermal conductivity of
the gas. The rate of heat transfer between the sidewall and the sample is taken to be
$\pi \kappa \sqrt{a \ell} (T_s-T)$ where $\ell$ is the length of the exposed tip. The temperature of the tip can be
found using

$$
T = \frac{P + \frac{\pi a^2 \kappa'}{L} T_0 + \pi \kappa \left[ \sqrt{a \ell} + a + \frac{a^2}{d} \right] T_s}{\frac{\pi a^2 \kappa'}{L} + \pi \kappa \left[ \sqrt{a \ell} + a + \frac{a^2}{d} \right]}
$$

(6.1)

where $L$ represents the length of the monolithic crystalline temperature sensor, $a$ its
radius, and $\kappa'$ its thermal conductivity. $P$ represents laser power dissipated in the
phosphor which corresponds to the absorbed power multiplied by the fraction of the
decay rate which is nonradiative.

The dependence of the phosphor tip’s temperature as a function of its distance
from the sample is presented in Fig. 6.2 by use of equation 6.1. The plots were
generated using the initial conditions of a sample surface temperature of $T_s = 100 \, ^\circ C$, a
connector temperature of $T_0 = 25 \, ^\circ C$ for the sensor probe, a total fiber probe length of $L = 10 \, cm$, a phosphor tip length and radius of $\ell = 1 \, mm$ and $a = 200 \, \mu m$ respectively, a thermal conductivity of $\kappa = 13 \, W/mK$ for YAG, and finally a thermal conductivity of $\kappa = 0.03 \, W/mK$ for air at approximately 100 °C. From each selected $P$, equation 6.1 yields one of the curves shown as the distance between the phosphor tip and sample is varied from 0.5 mm to approximately 10 μm in step sizes of 10 μm. When the phosphor tip temperature is below the sample surface temperature, the phosphor’s temperature shifts upward to a value towards that of the sample when approaching and touching the sample and inversely downward for phosphor temperatures above the sample surface temperature. This phenomenon is depicted in Fig. 6.2. The curves from the figure are anticipated to be symmetric about the true surface temperature of the sample for phosphor temperatures the same magnitude above and below the actual temperature as exhibited in the model. One must keep in mind that factors such as the sample’s profile, thermal conductivities of the sample and gas medium, and the degree of contact pressure will determine the magnitude of the shifts in any real situation.

Fig. 6.3 illustrates the temperature difference between the gap distances of 10 μm and 100 μm for each initial heating condition versus the initial heating temperatures at the specific gap distances of 10 μm (hollow circles) and 100 μm (squares). The dotted line in the Fig. 6.3 represents the linear best fit line for the gap distance of 10 μm and the dot-dash line signifies the best fit for the 100 μm gap. As depicted in the figure, where the linear best fit lines cross from negative to positive, the true surface temperature is revealed for both the contacting and noncontacting scenarios. The corresponding temperatures for which the contacting and noncontacting conditions crossed from
negative to positive in Fig. 6.3 were found to be 100 °C +/- 1.2x10^{-8} °C and
100 °C +/- 7.5x10^{-8} °C from the best fit lines, respectively.

A second technique to determine the actual surface temperature would entail
drawing straight lines through the data points which are closest to the sample surface for
each data set and extrapolating them to the left to find the corresponding common
intersection temperature. Fig. 6.4 exhibits the temperature of the phosphor at the specific
gap distances of 10 μm and 50 μm at various laser power dissipation values which were
extracted from Fig. 6.2. It can be seen in Fig. 6.4 that all the extrapolated lines intersect
at a common point. Calculations were performed using Matlab to determine the six
crossing temperatures for all six possible pairs. They showed 100.0043 °C and
99.9943 °C as the highest and lowest intersection temperatures, respectively, while the
total average temperature for all the intersections was found to be 99.9993 °C
+/- .0036 °C. Sample surface qualities and profiles vary to an assortment of degrees due
to diverse fabrication techniques. As a consequence, the minimum gap length will be
determined by the particular modus applied to create the sample surface. It is not
unreasonable to expect that a minimum gap length of 50 μm may apply for a rough
surface. The same numerical calculations for gap distances of 50 μm and 100 μm at the
same laser power dissipation values from Fig. 6.2 were performed. The four extrapolated
straight lines had a common intersection of 99.9996 °C. Variations in the intersection
temperature values for the four data sets for this case were only evident for values after 8
significant digits. Error in this technique would be minimized by investigating data sets
which are perfectly symmetric mirror images about a horizontal line going through the
true surface temperature.
As can be inferred from Fig. 6.4, one does not need to make contact with the sample to obtain exceptional results for samples with adequate surface profiles with the thermally compensated FDR sensor. This novel technique has the capacity of providing a noninvasive means of measurement of surface temperatures without perturbing the sample with extensive heat drain. This model will only hold for laser heating sources which have a high degree of stability.
Figure 6.2: Phosphor temperature versus gap length using the theoretical equation 6.1 with various laser dissipation values.
Figure 6.3: Phosphor temperature difference between the gap distances of 10 μm and 100 μm for each initial heating condition in Fig. 6.2 versus the initial heating temperatures at the specific gap distances of 10 μm (hollow circles) and 100 μm (squares).
Figure 6.4: Phosphor temperature versus gap length at various laser dissipation values using the theoretical equation 6.1 with the extractions of specific gap distances of 10 μm and 50 μm from Fig. 6.2. Extrapolation plots (dotted lines) are applied to each data set.
6.2 *Experimental Details and Results for the Thermally Compensated FDR Temperature Sensor*

In the effort to demonstrate the operation of the FDR sensor in the thermally compensated mode, the YbAG phosphor probe presented in the former section was chosen as the candidate for deployment in this endeavor. The YbAG phosphor was chosen specifically due to it exhibiting the maximum response (16 % change in decay rate for the first 100 °C) for the temperature range selected for this experimental test in comparison to the other phosphors investigated. Fig. 6.5 illustrates the experimental setup for the thermally compensated FDR test. A pulsed laser diode centered at 940 nm was employed as the excitation source for the Yb$^{3+}$ ions. The 50 μs excitation pulses at a repetition rate of 50 Hz were reflected off a dichroic filter (HR @ 940 nm, HT @ 1040 nm) and transmitted through a NIR polarizing beam splitter cube where the excitation pulses were parallel to the plane of incidence of the beam splitting face. The pulse train excitation source was kept at a duty cycle which prohibited any significant heating effects to the YbAG phosphor. A CW laser diode centered at 940 nm with orthogonal polarization was used in order to provide an internal mechanism of heating the YbAG phosphor. The 940 nm CW emission was normal to the plane of incidence to the beam splitting face of the NIR polarizing beam splitter cube. The polarized beams from the pulse train excitation source and the CW source are then coupled into a silica fiber which is mated to a 2 m patch cable via a SMA to SMA connector. The opposite end of the fiber patch cable was fixed to a SMA to SMA mating sleeve that was used to connect to the YbAG phosphor temperature sensor. The temperature probe measured approximately 10 cm in total length and had a diameter of 400 μm. The YbAG phosphor length at the end of the YAG lead fiber measured 1 mm in length with a diameter of
Figure 6.5: Schematic of the experimental layout for fiber optic thermally compensated YbAG temperature sensor.
400 μm. The tip of the YbAG phosphor was polished perpendicular to the growth axis to a good optical finish using diamond lapping films. The induced 1040 nm ytterbium fluorescence propagates back through the YAG lead fiber of the temperature probe and through the fiber patch cable. After exiting the patch cord silica mating assembly at the opposite end of the temperature probe, the beam was collimated by the plano-convex lens, transmitted back through the cube polarizer, and finally any scattered light is reflected by the dichroic filter while the fluorescence is transmitted. The fluorescence is collected by a silicon detector and then acquired by a digital signal averaging oscilloscope for analysis. A computer and digital signal processor was also employed for data acquisition and signal processing in order to obtain real time decay rate measurements.

The YbAG phosphor temperature probe was mounted onto an X-Y-Z stage in order to vary the gap distance between the phosphor tip and the sample surface of the hot plate which was oriented perpendicular to the growth axis of the probe. The X-Y-Z stage also provided a means to position the tip in close proximity to the sample surface region of interest. A multimeter was connected to a type E nickel-chromium vs. copper-nickel thermocouple which was adhered to the hot plate’s surface via high conductivity silver paint to monitor the surface temperature. The experiment was conducted in a plexiglass isolation chamber at 1 atmosphere (760 torr) of pressure in order to minimize any wind drift which would cause erroneous readings by the 25 μm diameter thermocouple used to monitor the surface temperature.

The YbAG phosphor temperature probe system was calibrated against a type S platinum-10% rhodium versus platinum thermocouple which was oriented horizontally in close proximity with the phosphor tip. The calibrations were performed as described in
the former sections for the other phosphor probes presented. A first order exponential fit curve \( t = 44.6 \, ^\circ C \) was used to make an acceptable fit to the calibration points for the first 140 \(^\circ C\) as divulged in Fig. 6.6. Each data point in the figure represents the average of five measurements. Each measurement consists of the average of 256 decay traces. All the data points were fitted by a single exponential over more than two e-foldings to determine the decay rate. The sample surface temperature was found to be 79 \(^\circ C\) +/- 2 \(^\circ C\) using the thermocouple that was fixed to the hot plate’s surface. Extensive experience of the decay rate measurements in this temperature region has shown typical errors of 0.2 \%. Fig. 6.7 displays the relative sensitivity of the YbAG phosphor for the low temperature end of interest for this experiment with a first order exponential decay fit \( t = 56.6 \, ^\circ C \) to the data points. At approximately 79 \(^\circ C\), a sensitivity value of 0.0015 /K is obtained corresponding to a calibration accuracy of better than 1.5 \(^\circ C\).

The measured temperature versus gap length for the YbAG phosphor sensor at various initial heating temperatures is presented in Fig. 6.8. The CW laser diode current driver was varied in order to dissipate various laser powers into the phosphor tip. Power transmission measurements disclosed that approximately only 2.30 \% of the launched laser power in the YbAG sensor was transmitted through the tip of the phosphor. The diode currents of 0 A, 0.6 A, 0.65 A, 0.70 A, 0.75 A, and 0.85 A were calculated to correspond to 0 mW, 98 mW, 130 mW, 169 mW, 202 mW, and 274 mW of launched laser power into the phosphor tip, respectively. Due to ytterbium ions being primarily radiative, it is expected that only about 10 \% of the calculated launch powers will actually be converted to thermal energy. In any event, the corresponding launch powers should be sufficient for the temperature range to be inspected in this endeavor. Each data point in
Figure 6.6: Low temperature fluorescence decay rate versus temperature for the YbAG phosphor.
Figure 6.7: Relative sensitivity of the YbAG sensor between room temperature and 140 °C.
the figure is the average of 20 consecutive decay rate measurements which were converted into the corresponding temperature reading using the calibration chart presented in Fig. 6.6.

It is seen that for initial heating temperatures below the actual surface temperature, which reflects the 98 mW and 130 mW laser launching powers, result in the proliferation of the YbAG phosphor’s temperature rose upon contact with the surface. Conversely, for the initial temperatures above the actual surface temperature, corresponding to the 169 mW, 202 mW, and 274 mW laser launching powers, a decrease was detected in the YbAG phosphor’s temperature upon contact. It is quite apparent the smallest change experienced by the phosphor’s temperature pertained to the case where the initial heating temperature was closest to the true surface temperature. This is delineated by the 169 mW case in the figure. When the YbAG sensor was not operated in the thermally compensated mode, the phosphor’s temperature was found to be approximately 27 °C below the surface temperature when contact was made. It is not unreasonable that the error bars can be abated providing that the surface temperature of interest remains stable for an extended period of time. The nominal surface temperature of 79 °C for this project was found to vary by +/- 2 °C within a 10 minute heating-cooling cycle. The experimental data presented in Fig. 6.8 echoes the model presented in Fig. 6.2.

The smallest two gap distances from each data set in Fig. 6.8 excluding the case when no internal heating was applied (0 mW launch power case) are presented in Fig. 6.9. The smallest gap distance for each data set is 0 μm in which the phosphor tip is abutting the surface of the hot plate. In reality this would correspond to a gap distance of approximately 50 μm or so due to the semi-nodular surface which the hot plate’s surface
Figure 6.8: Experimental data of the phosphor temperature versus gap distance for various launching laser dissipation values of the YbAG phosphor.
is composed of. In any event, linear extrapolations were applied in the effort to investigate the temperature at which each data set intersected with the others similar to the exercise introduced in Fig. 6.4. These calculations divulged 72.21 °C and 84.73 °C as the highest and lowest intersection temperatures, respectively, while the total average of all the intersections amongst all the data sets was determined to be 79.74 °C +/- 4.35 °C. This experimental value obtained agrees remarkably with the 79 °C average temperature reading obtained from the thermocouple fixed in the same proximity of the sample surface. It is inferred that the proper modus to apply the extrapolation intersection method to find the true surface temperature is to use two curves which are mirror images about a horizontal line through the true surface temperature. This would provide two data sets with approximately equal slopes in magnitude. In Fig. 6.9, this would represent the 98 mW and 202 mW launching cases. The extrapolation intersection temperature for this corresponding case is 79.15 °C.

The temperature difference between the gap distances of 0 μm and 100 μm for each internal heating data set in Fig. 6.8 versus the initial heat temperatures for each specific gap distance is presented in Fig. 6.10. Calculation of the intersection temperature from the linear best fit lines for the contacting condition (dotted line fitted to hollow circles) and noncontacting condition (dash-dot line fitted to squares) disclosed a intersection temperature of 80.167 °C. The crossing intersection from negative to positive in the figure for the contacting and noncontacting conditions was found to be 80.49 °C +/- 1.29 °C for both respective conditions. As exemplified from the figure, this technique also provides a dexterous means in calculating accurate surface temperatures for a fluorescence decay phosphor sensor operated in the thermally compensated mode.
Figure 6.9: Phosphor temperature versus gap length at various launching laser dissipation values extracted from Fig. 6.8 for specific gap distances of 0 μm and 100 μm. Extrapolation plots (dotted lines) are applied to each data set.
Figure 6.10: Phosphor temperature differences between the gap distances of 0 μm and 100 μm for each internal heating data set in Fig. 6.8 versus the initial heat temperatures for each specific gap distance of 0 μm (hollow circles) and 100 μm (squares).
A few implications may be implemented to accomplish the task of minimizing the measurement uncertainty using this thermally compensation technique. First the surface of interest should have the most uniform temperature profile with minimum transient and steady-state temperature disturbances as possible to reduce measurement error for any gap distance temperature reading by the sensor. This criterion is extremely substantial in the extrapolation exercise used to inspect the intersection temperatures amongst the various initial heating temperatures of the phosphor. Secondly, any fluctuations from the internal heating source must be minimized for steady-state heating of the phosphor tip. Finally, idealistically one would desire to operate the thermally compensated fluorescence decay rate sensor at initial heating temperatures with the same magnitude temperature offsets above and below the actual surface temperature to be inspected. This would provide the harvest of a series of symmetric curves above and below the true surface temperature for the extrapolation exercise to be applied. For gaseous media which are more thermally conductive opposed to the conditions used in this experiment, one would experience a decrease in the immensity of the shift in the phosphor temperature as the gap length is contracted.
CHAPTER 7

CONCLUSION

In the course of this research there was successful demonstration in the improvement of the sensitivity of Yb:YAG based fluorescence decay rate temperature sensors. Long term stability tests performed unveiled these sensors as premier candidates to long term deployment in applications such as coal gasifiers, plasma/microwave processing, and a multitude of diverse industries. Pairing analysis of various rare earth elements with ytterbium in different ratios disclosed improved response all the way down to room temperature which was nonexistent in our previous studies. The various codoped phosphor studies provided insight on applicable combinations to suit the response needs for specific process temperature ranges that may be needed in various technologies that may exist currently and that may develop in the future.

Accurate surface temperature measurements were achieved by operating a sensor in the thermally compensated mode for the first time. This novel technique is envisioned to be welcomed in plasma processing, microwave processing, and rapid thermal processing industries. With the combination of their inertness to electrically hostile environments, durability for long periods of time at elevated temperatures, and temporal response, this new technique could have significant economic impact in downtimes plaguing many industries. The thermally compensated sensor should be suitable for critical temperature measurements in which the actual surface temperature of a sample is sought, by virtually extinguishing thermal drain loss currently experienced by
thermocouples.

Future work should be directed toward application of the thermally compensated fluorescence decay rate sensor to elevated temperatures to conform to the needs of rapid thermal processing and other industries requiring accurate surface temperature measurements. It would be interesting to see this technique implemented to other hosts and fluorescing ions as well in order to verify the applicability of this novel method to other hosts. The methodology outlined in this dissertation is appropriate for the temperatures for which this work was applied.
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APPENDICES
Appendix A: Fluorescence Stability

Figure A.1: 12 hour fluorescence decay rate data for 10%Yb:YAG phosphor at 1,118 K +/- 1.8 K.
Figure A.2: 12 hour fluorescence decay rate data for 10% Yb:YAG phosphor at 1,215 K +/- 2.0 K.
Appendix A: (Continued)

Fluorescence Decay Rate (/s)

Time (Hours)

Figure A.3: 12 hour fluorescence decay rate data for 10%Yb:YAG phosphor at 1,311 K +/- 2.2 K.
Appendix A: (Continued)

Figure A.4: 12 hour fluorescence decay rate data for 10\%Yb:YAG phosphor at 1,399 K +/- 1.6 K.
Figure A.5: 12 hour fluorescence decay rate data for 10%Yb:YAG phosphor at 1,483 K +/- 2.3 K.
Appendix A: (Continued)

Figure A.6: 12 hour fluorescence decay rate data for 10%Yb:YAG phosphor at 1,575 K +/- 5.4 K.
Figure A.7: 12 hour fluorescence decay rate data for 10% Yb:YAG phosphor at 1,665 K +/- 2.0 K.
Figure A.8: 12 hour fluorescence decay rate data for 10%Yb:YAG phosphor at 1,686 K +/- 2.6 K.
Appendix A: (Continued)

Figure A.9: 12 hour fluorescence decay rate data for 20%Yb:YAG phosphor at 1,118 K +/- 1.9 K.
Figure A.10: 12 hour fluorescence decay rate data for 20\%Yb:YAG phosphor at 1,221 K +/- 1.5 K.
Figure A.11: 12 hour fluorescence decay rate data for 20%Yb:YAG phosphor at 1,317 K +/- 2.6 K.
Appendix A: (Continued)

Figure A.12: 12 hour fluorescence decay rate data for 20%Yb:YAG phosphor at 1,403 K +/- 2.9 K.
Figure A.13: 12 hour fluorescence decay rate data for 20%Yb:YAG phosphor at 1,490 K +/- 2.0 K.
Figure A.14: 12 hour fluorescence decay rate data for 20%Yb:YAG phosphor at 1,571 K +/- 2.8 K.
Appendix A: (Continued)

Figure A.15: 12 hour fluorescence decay rate data for 20%Yb:YAG phosphor at 1,661 K +/- 1.9 K.
Figure A.16: 12 hour fluorescence decay rate data for 50%Yb:YAG phosphor at 1,124 K +/- 1.2 K.
Figure A.17: 12 hour fluorescence decay rate data for 50%Yb:YAG phosphor at 1,221 K +/- 1.8 K.
Figure A.18: 12 hour fluorescence decay rate data for 50%Yb:YAG phosphor at 1,316 K +/- 2.2 K.
Figure A.19: 12 hour fluorescence decay rate data for 50%Yb:YAG phosphor at 1,406 K +/- 1.9 K.
Figure A.20: 12 hour fluorescence decay rate data for 50%Yb:YAG phosphor at 1,495 K +/- 2.7 K.
Appendix A: (Continued)

Figure A.21: 12 hour fluorescence decay rate data for 50%Yb:YAG phosphor at 1,581 K +/- 2.8 K.
Figure B.1: Schematic model for thermal transport between the phosphor tip and sample.
Appendix B: (Continued)

The temperature profile of the phosphor depends upon the rate of its internally generated heat (via CW 940 nm radiation), its capacity to store this heat, and the rate of thermal conduction to its boundaries (where heat is transferred to the surrounding environment). Thermal transport between the tip and sample can be demonstrated by calculating the approximate thermal resistance ($T.R_{tip}$) from the formula

$$T.R_{\text{Tip}} = \int \frac{1}{A \kappa} dx$$

$$T.R_{\text{Tip}} = \int_{0}^{d} \frac{1}{\pi \kappa (x + a)^2} dx, \text{note: } \frac{d}{dx} \left( \frac{1}{x} \right) = -\frac{1}{x^2}$$

$$T.R_{\text{Tip}} = \frac{1}{\pi \kappa} \left[ \frac{1}{(d + a)} - \frac{1}{a} \right]$$

$$T.R_{\text{Tip}} = \frac{1}{\pi \kappa} \left( \frac{d}{a(d + a)} \right)$$

(B.1)

where $A$ is the cross-sectional area of the inverted frustum, $a$ the radius of the inverted frustum at the base (at phosphor tip), $d$ is the gap distance between tip and sample, $(a+d)$ the radius of the frustum at the top (at surface of interest) and $\kappa$ is the thermal conductivity of the gas as shown in Fig. B.1. The reciprocal of the thermal resistance ($T.R_{tip}$) yields the thermal conductance ($T.C_{tip}$), thus

$$T.C_{\text{Tip}} = \pi \kappa a \left( 1 + \frac{a}{d} \right).$$

(B.2)

In an effort to approximate the rate of heat transfer between the sample and the sidewalls of the phosphor tip, we assume the length of the sidewall to participating in thermal transport from the end of the phosphor tip to be approximately $2\ell$. The sidewall area is calculated by
Figure B.2: Schematic model for thermal transport between the phosphor sidewalls and sample.
Appendix B: (Continued)

\[ 2\pi rl = 2\pi a 2\ell = 4\pi a \ell \]  \hspace{1cm} (B.3)

where \( \ell \) is the length of the phosphor tip referring to Fig. B.2.

The area of the sample of interest considered to participate in thermal transport with the sidewall is that of a disk with radius \((d + \ell)\) and is intercepted at 45° with the sidewall surface. The corresponding area is given by

\[ \pi r^2 = \pi (d + \ell)^2 \]  \hspace{1cm} (B.4)

where \( d \) is the gap distance referring to Fig. B.2. The geometric mean area is found to be the square root of the product of Eq. B.3 and Eq. B.4, giving

\[ \sqrt{4\pi^2 a \ell (d + \ell)} = 2\pi \sqrt{a \ell (d + \ell)}. \]  \hspace{1cm} (B.5)

Thermal resistance \((T.R.\text{Side})\) for the sidewalls can be approximated by

\[ T.R.\text{Side} = \int \frac{1}{Ak} dx \]

\[ T.R.\text{Side} = \int_0^d \frac{1}{2\pi \sqrt{a\ell (x + \ell)}} dx = \frac{1}{2\pi \sqrt{a\ell}} \int_0^d (x + \ell)^{-1/2} dx \]

yielding the semi-quantitative result of

\[ T.R.\text{Side} = \frac{1}{2\pi \sqrt{a\ell}}. \]  \hspace{1cm} (B.6)

Taking the reciprocal to approximate the thermal conductance \((T.C.\text{Side})\) gives

\[ T.C.\text{Side} = 2\pi \sqrt{a\ell}. \]  \hspace{1cm} (B.7)

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The heat equation following from the conservation of energy is

\[
\begin{bmatrix}
\text{Heat} \\
\text{Conducted}
\end{bmatrix}_{\text{In}} + \begin{bmatrix}
\text{Heat} \\
\text{Generated}
\end{bmatrix}_{\text{Within}} = \begin{bmatrix}
\text{Heat} \\
\text{Conducted}
\end{bmatrix}_{\text{Out}} + \begin{bmatrix}
\text{Internal} \\
\text{Energy}
\end{bmatrix}_{\text{Change}} \tag{B.8}
\]

where the heat conducted in will be through the phosphor end and the sidewall of length \(2\ell\) from Eq. B.2 and Eq. B.7 respectively, the heat generated within will be from a CW 940 nm heating source represented by \(P\) for our system, and the only mechanism of heat loss considered is to be along the length of the probe lead fiber given by

\[
\frac{\pi a^2 \kappa'}{L} (T - T_0) \tag{B.9}
\]

where \(L\) is the length of the lead fiber, \(T_0\) the temperature of the heat sink at the end of the YAG lead fiber and \(\kappa'\) the thermal conductivity of the YAG lead. We assume that the phosphor has a uniform temperature \(T\) which sets the change in internal energy to zero.

Applying these assumptions to Eq. B.8 generates the heat equation pertaining to our system which is given by

\[
\pi \kappa a \left( 1 + \frac{a}{d} \right) (T_S - T) + \pi \kappa \sqrt{a \ell} (T_S - T) + P = \frac{\pi a^2 \kappa'}{L} (T - T_0). \tag{B.10}
\]

Solving Eq. B.10 for \(T\), the temperature of the phosphor tip can be obtained from the formula

\[
T = \frac{P + \frac{\pi a^2 \kappa'}{L} T_0 + \pi \kappa \left( \sqrt{a \ell} + a + \frac{a^2}{d} \right) T_s}{\frac{\pi a^2 \kappa'}{L} + \pi \kappa \left( \sqrt{a \ell} + a + \frac{a^2}{d} \right)} \tag{B.11}
\]
About the Author

Jermaine L. Kennedy received a B.S. in Physics in 1998 and a B.S. in Secondary Education in 1999 from the State University of New York at Buffalo State. In 2001 he completed a M.S. in Physics from the University of South Florida in 2001.