Spring 2023

Expanding Upon Excitation: The Observance of Nonlinearity in Alexandrite

Katherine A. Stephens
katherine_stephen57@mymail.eku.edu

Eastern Kentucky University

Expanding upon Excitation: The Observance of Nonlinearity in Alexandrite

Honors Thesis

Submitted

in Partial Fulfillment

of the

Requirements of HON 420

Spring 2023

By

Katherine Stephens

Faculty Mentor

Dr. Thomas Jarvis

Department of Physics, Geosciences, and Astronomy

Expanding upon Excitation: The Observance of Nonlinearity in Alexandrite

Katherine Stephens

Dr. Thomas Jarvis

Nonlinear optical effects are a light-matter interaction that can be observed when multiple optical fields drive a response in the material under excitation. To determine whether or not an effect is present in alexandrite, a beryl stone doped with chromium ions, literature reviews were conducted and research regarding the theory around the nonlinear multiphoton was performed. Safety measures for the laboratory and previous research using the same laser were also examined. This was taken into account when performing original experiments to measure a potential effect from a laser interaction with alexandrite. After an initial experiment was adjusted to filter out background noise, the secondary experiment provided results that were graphed as Second Harmonic Fluorescence Photovolate as a Function of Relative Input Power and deemed quadratic. The possibility of a nonlinear multiphoton effect being present in alexandrite crystals is discussed.

Keywords: alexandrite, laser, multiphoton effect, nonlinear multiphoton effect, nonlinearity, optics, quantum physics, physics

Table of Contents

Page

List of Figures

Page

List of Illustrations

Page

Acknowledgments

I would like to thank my mentor, Dr. Thomas Jarvis, for his constant support, advice, and encouragement throughout this project. His unwavering faith in my abilities allowed me to accomplish this project, and his excitement for this experiment gave me the motivation to continue the process after this thesis is complete. I would also like to thank the members of the Physics, Geosciences, and Astronomy department at Eastern Kentucky University for their kindness and for welcoming me into the department, my friends and family for their emotional support during my academic career, and the EKU honors department for allowing me to explore this fantastic research opportunity.

Introduction

Alexandrite

Figure 1: Russian Alexandrite Sample Color Change under Daylight (Left) and Fluorescent Light (Right)

Alexandrite is a variety of beryl that is highly valued in the jewelry industry for its rarity and the unique color-changing property that it exhibits. In outdoor and fluorescent lighting, the stone often appears a bluish-green color (Figure 1, left)[1]. Under incandescent lighting, it takes on a purple or red coloration (Figure 1, right)[1]. The reason this gemstone is able to change colors under different lighting is because of the optical properties of the chromium (Cr^{3+}) ion chromophores present in the beryl crystal matrix. These ions cause what is known as the alexandrite effect, which was first observed in the 19th century[2]. Other chromium-rich

stones can have this effect as well, where the color of the material can change from a shade of red to a shade of green under different lighting conditions.

While alexandrite has cosmetic value as a decorative gemstone for use in jewelry, it can also be used in a laser. Alexandrite lasers are typically used in dermatology due to the longer wavelengths that it can emit in comparison to certain other common lasers, which in clinical trials has been shown to have a reduced impact on the skin when used for treatment[3]. However, other types of lasers – such as the titanium: sapphire solid-state laser – can be tuned to emit at the same wavelength as alexandrite sources, so there may be other reasons that this type of laser is used over all others. It can be assumed that the reason behind the almost exclusive use of alexandrite lasers in dermatology is due to a negative association with other types of lasers in the field of safety, and using a different material may assist in reducing the apprehension around using laser treatment methods – after early clinical results with alexandrite lasers, researchers developing subsequent dermatological therapies may have seen the alexandrite laser as a safe default that would not present challenges in institutional review or clinical safety requirements.

Lasers

There are many different iterations of the laser using different materials. Gas lasers commonly use neutral atoms like helium and neon, ions such as argon, excimers that use an excited dimer gas molecule, and metal vapors (helium-cadmium or helium-mercury lasers) and utilize either optical pumping or discharge excitation[4]. Solid-state lasers can utilize a large variety of different materials to produce a beam, such as ruby and titanium-doped sapphire, with an interaction of laser-active ions and the host lattice necessary for

laser light wavelengths to be emitted[5]. Diode lasers are pumped by an electrical current and are often used to excite a gain medium in other kinds of laser systems as well[6]. Lasers are used for an enormous variety of different uses in the present age. Some common uses include hair[7] and tattoo[8] removals, as well as medical uses for the treatment of keratosis pilaris[3] and surgical procedures[9]. While these applications have a commonplace role today, the original invention of the laser was a revolutionary development. Before the initial creation of the laser, a "maser", standing for "microwave amplification by stimulated emission of radiation", was the only available method of creating high-powered beams of electromagnetic waves[10]. While these produce intense beams of microwaves, physicists of the time wanted to produce a powerful beam of coherent light at optical wavelengths, where the photon energy is much higher than that of a microwave beam. In the 1960's, Theodore Maiman published a very brief article reporting his invention of the laser using ruby[11]. This new instrument allowed entirely new fields of physics to be developed that could study phenomena that were previously inaccessible – perhaps most significantly, allowing the study of otherwise inaccessible problems in quantum physics. The light from the laser opened new opportunities for researchers to observe phenomena that previously could only be theorized, including the work of Maria Göppert-Mayer in 1931[12].

Theory

In her work, Göppert-Mayer suggested a phenomenon that works around what appears to be a restriction of quantum mechanics. It was thought that the quantum states that an electron could go through must be separated by specific energy gaps determined by the potential energy the electron experiences, rather than by arbitrary amounts of energy. Göppert-Mayer suggested that an electron can, in fact, move between quantum states in multiple steps if the quantum mechanical pathway still resulted in the same energy difference between the initial and endpoint states. This theory was dubbed the nonlinear multiphoton effect. Unfortunately, the observation of these effects can only emerge with extremely powerful light in a narrow-band spectrum[13], something which she did not have a way to produce at the time. Soon after Maiman's invention of the laser, Göppert-Mayer's theory was expanded upon by multiple physicists, including Kleinman's paper on how to test her theory with the newly invented laser[14] and Kaiser and Garrett's experiment utilizing her theory[15]. The nonlinear multiphoton effect can be elaborated upon by Abella in his observations in cesium vapor providing the most elegant, and challenging, test of multiphoton absorption to that point[16].

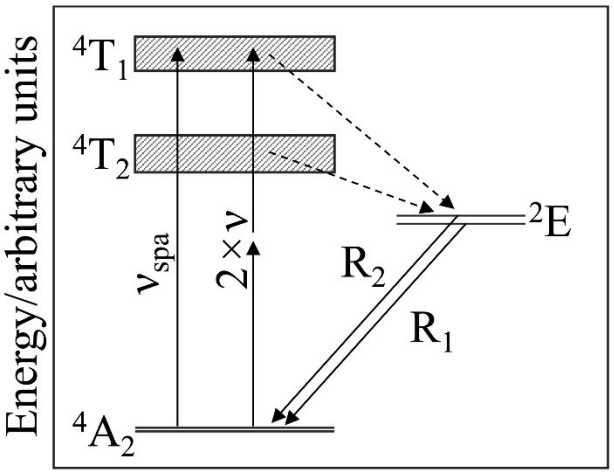

Figure 2: Simplified diagram for the Cr^{3+} ion in ruby. Solid lines indicate optical transitions, including a single-photon absorption from the ground state $^4A_2$ to upper absorption band $^4T_1$ (marked ν_{spa}), and two-photon absorption connecting the same states (labeled 2 x ν), and the 694 nm fluorescence emission, R_1 and R_2, from metastable state ^2E to the ground state. Dashed lines indicate non-radiative transitions from the absorption bands to ^2E.

The theory of multiphoton processes can be explained by considering the energy levels through which the photon moves in a transition between quantum states (Figure 2)[17]. This

figure illustrates a nonlinear, multi-photon transition in ruby, which was observed using femtosecond laser pulses in our laboratory last year. The fundamental optical physics that underly that process can be expected to be similar for alexandrite, or enough so for an illustrative purpose. Ruby was chosen as the first material to study in this line of inquiry because the Cr^{3+} ions in that mineral have little interaction with the surrounding crystal matrix, and the quantum mechanical states available to electrons in those ions are therefore not significantly affected by interaction with the host sapphire; the behavior of Cr^{3+} ions in the chrysoberyl matrix of alexandrite is expected to be largely similar. Under normal thermal conditions at room temperature, an electron begins at the ground state and can become excited by a light-matter. In a normal single-photon process, this electron will move to the excited state briefly, then decay rapidly to the secondary excited state by emission of a phonon, which is the quantum mechanical description of a vibration, or can also be thought of as the emission of heat into the crystal, and finally decay back down to the ground state after an extended lifetime in the meta-stable state. This takes only a few milliseconds in ruby, and it is likely even less time in alexandrite. However, in a multiphoton process, this initial excitation is driven by two or more photons, while resulting in the same end state for the excited electron[18]. Morgenshtern and Neustruev were first able to determine that this phenomenon does occur in ruby, rather than a sequential process of single-photon absorptions [19]. Contrary to what may be suggested by the energy level diagram, however, the excited electrons do not rest in between energy levels – that is impossible. Rather, one could think of the energy level structure as an elevator, in that the

electron must end on one floor or the other with no option in-between. The output of both the single-photon and multiphoton effects in this model are approximately the same and can be virtually indistinguishable due to variation in the input power. Because of this, a method is needed to determine whether or not the output signal is a nonlinear multiphoton effect or a fast single-photon effect. The strength of the fluorescence emission that is given off when the multiphoton-excited electrons spontaneously decay to return to the ground state is proportional to the two input optical field intensities (Illustration 1). If these two intensities actually come from the same source, then their effect can be combined into a single excitation intensity, appearing bi-linearly (Illustration 2). Because both of the excitation sources are the same, the output signal would be proportional to the

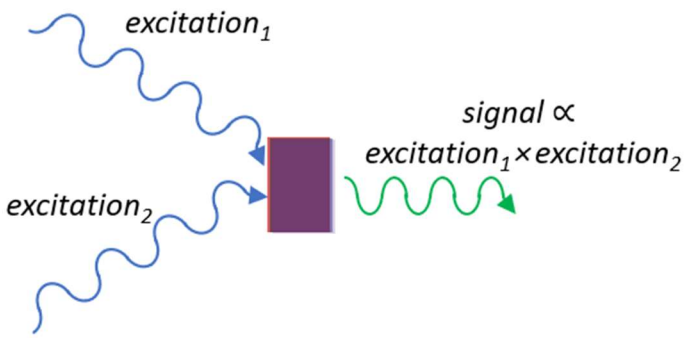

Illustration 1: Illustration of Wavelength Sources Passing Through a Sample and Creating a Signal Proportional to the Combined Wavelengths

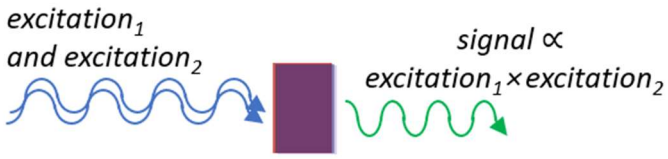

Illustration 2: Illustration of Wavelengths from the Same Source Passing Through a Sample and Creating a Signal Proportional to the Combined Wavelengths

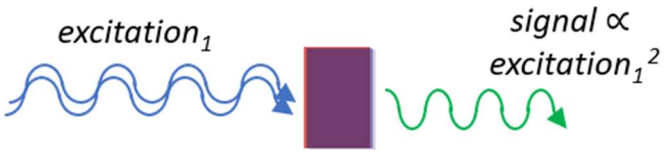

Illustration 3: Illustration of Wavelengths from the Same Source Passing Through a Sample and Creating a Signal Proportional to the Wavelength Squared

excitation squared (Illustration 3). This relationship allows for one to observe a quadratic relationship in a multiphoton effect rather than a linear relationship that would be present in a single-photon absorption.

Another aspect of optical physics involved in this application of Göppert-Mayer's multiphoton process theory is the effect of excitation with continuous lasers versus pulsed lasers (Figure 3)[17]. A continuous laser emits monochromatic light and can be thought of as a simple kind of laser where the light is always on, always oscillating at the same single frequency. A pulsed laser requires more wavelengths to be present in its spectrum as the pulse durations decrease. More wavelengths, which is to say more spectral bandwidth, are required to create a more complicated form of light[20], turning an oscillating electromagnetic field on and off in extremely short duration pulses. Again, the figure

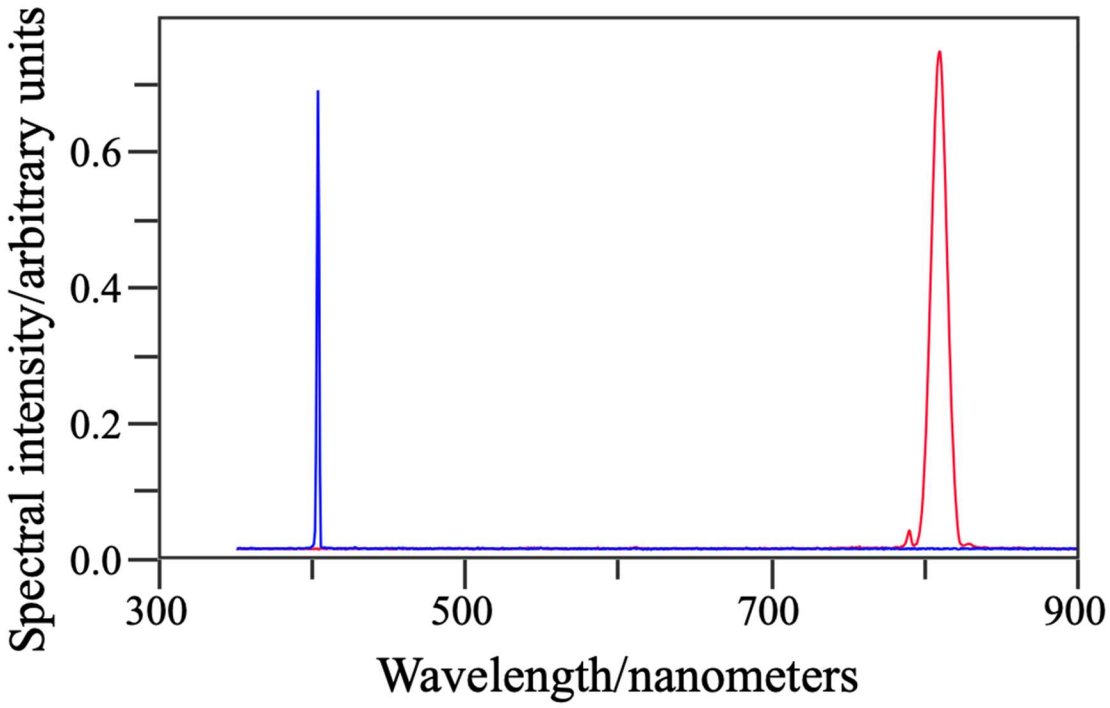

Figure 3: Typical spectra of two sources used to excite the Cr^{3+} ion in ruby. The feature at 404 nm (in blue) is the spectrum of a cw 405 nm laser diode module. The feature at 809 nm (in red) is a fs laser pulse with approximately 12 nm of bandwidth.

shown here demonstrates this principle for experiments in ruby, but it is assumed that similar optical physics would be explain our results for measurements in alexandrite, or similar enough to provide a baseline for purposes of comparison.

Because power is defined as energy over time, reducing the duration of pulses that deliver a constant amount of energy will increase the power. While the optical power could also be increased by raising the energy level, this can be difficult and become hazardous. The first observations of multi-photon processes, noted above, used millisecond laser pulses, but consequently still required sufficient energy that each pulse could ionize the air or destroy the target samples. By performing nonlinear optical measurements with femtosecond duration laser pulses, or more commonly referred to as "ultrafast lasers", it is possible for us to observe strong nonlinear effects that depend on the square of the optical excitation intensity without using problematically high pulse energies [21].

The significance of this effect can be observed in scientific uses for various fields. Multiphoton effects are used for types of microscopy and temperature-sensing using crystal fibres[22]. The effect is critical for the distributed sensing of temperatures, and this process can allow for temperature monitoring in different indoor environments. The geometry of the crystal fiber is an important aspect of this technique, and the effect allows for a very thin fiber to be used in this.

Literature Analysis

Kleinman's *Laser and Two-Photon Processes* review paper provides a look at the kinds of physics were newly accessible at the time of the invention of the laser. The laser can

then give researchers an intense source of coherent light that did not exist before, producing what can be thought of as a large number of identical photons. Kleinman's work gives a very broad understanding of what the term "nonlinear" means in optical applications, as well as the use of the new ruby laser for experimental tests of physical theory. His work observes two processes, Raman and two-photon, to support the statement that the presence of higher energy bands would explain the existence of a hidden intermediate stage where photons can instantaneously pause in a two-photon effect[14].

Kleinman uses Göppert-Mayer's paper as a base for his own suggested line of experimentation. The invention of the laser makes Göppert-Mayer's theory testable for the first time, and Kleinman explicates how such tests should be performed in order to get conclusive results. His paper goes into detail about each nonlinear process, Raman and two-photon, but subsequently reaches the conclusion that the Raman version of the proposed test experiments may be more difficult to perform than the two-photon measurements. Remarkably, by the time Kleinman had written this significant paper, the effect of two-photon absorption had already been observed in Europium-doped calcium fluoride crystals by an experimental group that was outpacing theoretical work at the time. Kleinman neglects any other explanation of the observed phenomena besides his own application of Göppert-Mayer's theory, which could have resulted in an incorrect conclusion; however, both processes were theoretically explained consistent with known optical physics[14].

Kleinman's paper provides a clear outline of how to perform the experiments that I will be conducting in my own research. While it is based heavily on Göppert-Mayer's work, it

provides a clear visualization of how a definitive experiment may be set up. It also provides support for Göppert-Mayer in stating that the experiment she had thought of should work for both processes with the use of a laser. Kleinman's work allowed for the testing of this circumstance to be understood in the sense of why it would work as needed.

Maria Göppert-Mayer published her direct research on the interaction of two light quanta with quantum systems with four different diagrams explaining how the light-matter interaction would proceed. Her thesis is that one should be able to observe the same kinds of results as the well-known Stokes and anti-Stokes Raman effects using double-absorption or double-emission of a photon. She uses theoretical analysis and mathematics for this paper, as she did not have the proper equipment to perform this experiment at the time, when no sufficiently intense source of coherent light existed. Göppert-Mayer relies on the conservation of energy in her theory, and her work allows for the assumption of an intermediate state where excited electrons can absorb another photon to reach the desired state[23].

Göppert-Mayer uses recently developed quantum mechanical theory to explain her own depiction of an intermediate state in excitation levels. She uses her own diagrams to show her process as well and compares her predicted outcome to that of the known Raman products. While her paper provides a foundation for many future experiments that probe quantum mechanical energy levels, she was unable to perform such experiments herself, which limits this work to the purely theoretical. She did not have the necessary materials to perform her theory, as optical technology was not yet sufficiently advanced to permit the observation of optical effects that depended nonlinearly on excitation power. Göppert-

Mayer's diagrams also ignore the conservation of momentum involved in the process, but this is acceptable due to the negligible effect this would have on the transition overall, where the miniscule photon momentum could easily be accounted for in atomic, molecular, or condensed matter systems. Her focus on the inelastic process takes into consideration the energy of the quantum emitter in the system, which is the focus of the Raman effect as well[23].

This work gives a basic outline of how to measure the intermediate stage process. By using two photons in her theory, Göppert-Mayer allows for the observation of the nonlinear aspect of quantum mechanical transitions to be understood, as well as a baseline for other physicists for experiments that could be performed and elaborated further upon.

Kaiser and Garrett's experiment report explains the two-photon process using optical masers, as the newly invented laser would be known for some time. They go into detail regarding the physical experiment performed, as well as the instruments used to observe the desired outcome. The two authors reach the conclusion that a two-photon process works in the way that Göppert-Mayer and Kleinman expected it to, and that the fluorescence observed was a result of the photons reaching the excited state by that nonlinear absorption pathway. This was supported by the presence of two different signals from photomultipliers appearing on an oscilloscope at the same time. Overall, Kaiser and Garrett found that the two-photon effect does work the way it was theorized to[15].

This report uses the direct findings of a physical experiment to support its thesis. Kaiser and Garrett include the graph and equations to further prove their work was accurate, as well as citing multiple other sources in their work to explain the different phenomena

occurring in their experiment. This source provides strong evidence as a primary source, as well as explaining how the experiment was conducted in a way that it could be replicated. However, it only observes the effects of the two-photon process in Europium-doped calcium fluoride crystals, and while this may be seen as a limitation, this first experiment opened the doors for many similar experiments to take place and improve the research on this specific effect with different crystals and other optical materials [15].

Kaiser and Garrett reference both Göppert-Mayer and Kleinman in their paper, as Göppert-Mayer developed the first multiphoton transition theory, and Kleinman gave additional support on how a definitive experiment should be conducted. This paper explains what will need to be recorded for similar experimentation as well as what the results can be compared to when, for instance, using alexandrite rather than europium-doped fluoride crystals. It names instruments that can be used, or the modern version of these instruments, and provides a basic description of what a similar physics experiment should entail.

Serway and Jewett provide in the textbook Physics for Scientists and Engineers an educational overview of many different aspects of physics, including quantum mechanics and its applications. The content provided allows students to understand photoelectrons, electromagnetic waves, the wave and particle properties of light, and quantum effects. By giving examples of these phenomena and encouraging students to use practice problems that are provided in the text, as well as explaining how previous physicists made their discoveries on material related to the subjects, Serway and Jewett support a comprehensive understanding of many different aspects of physics, including quantum physics[24].

Serway and Jewett use equations discovered in physics research to explain the concepts given. These equations were determined by many different scientists in the past, such as Louis de Broglie, Max Planck, and Erwin Schrödinger. Serway and Jewett use logic and previously determined knowledge to make connections between concepts and teach students in a way that is readily understandable at the appropriate level. The text also uses previously worked examples to prove that the given methods work the way they are intended to. This book, however informative, does admit that there are unknowns still present in physics, such as those regarding the duality of light. Light acts as both a particle and a wave depending on the circumstances, and this has caused confusion in the physics community for a long time. It acknowledges that theories are still theories and should be treated as such rather than pure fact. Serway and Jewett also provide a summary of the basic principles at the end of each chapter to ensure that the reader understands the concepts of the material[24].

Serway and Jewett provide a textbook that is immensely helpful in the study and understanding of the basic background physics necessary to undertake the study of nonlinear multiphoton optics. They give basic definitions of many of the concepts that would be involved, as well as acknowledge the difficulties that may come with physics research. This text provides an advanced understanding of physics in a way that some other texts may not be able to, which was be highly beneficial to this research. It can be used as a baseline to build upon in the nonlinear studies by providing the limitations and uncertainties involved with optics, as well as the nonlinear process basics and what equations can be used to determine measurements.

Thornton's *Modern Physics for Scientists and Engineers* compiles an incredible amount of information regarding physics into the textbook in a way that is understandable to students with limited knowledge of the subject. This text provides students a basic understanding of many different aspects of modern physics, such as the quantization of energy levels, atomic theory, and quantum numbers. The textbook provides a large number of equation examples and diagrams to explain the material gathered from years of research by many physicists, such as Wilhelm Röntgen, Ernest Rutherford, and Pieter Zeeman[25].

Thornton provides many diagrams, equations, and examples to act as proof that the discoveries previously made by other physicists remain valid. He uses logical reasoning and known equations to make new connections, as well as previously established connections between aspects of physics. These connections also establish that these discoveries are intellectually coherent in a way that allows the use of the equations provided to predict outcomes of interest. The text also goes into depth on how physicists in the past were able to make the discoveries that are mentioned in the book, which allow for a model of how to perform certain experiments. He also considers poorly established models that had been previously made, and the fact that many discoveries are based on theory, both of which can act as a sort of reassurance that physicists are still adapting their understanding of certain aspects. This textbook provides learning checks to ensure that the students understand each concept and can check their work before moving ahead[25].

This textbook provides many helpful resources, such as models of electrons and energy levels. These will come into play with the manipulation and measurements of multiphoton optics and the emission of photons; Thornton specifically emphasizes the hydrogen atom,

which is often used as a model for atomic systems, including the absorption and emission of light. By comparing the hydrogen model to that of the atoms involved in laser research, the models can act as an example of what should be expected from experimentation. This source builds upon other physics textbooks in the detail that is given on specific subjects, which in other books may be lacking. It can be used as a base knowledge point for the understanding of energy involved in quantum physics, while also using other sources as evidence within its own content.

Benton's work *A Proposed Method for a Photon-Counting Laser Coherence Detection System to Complement Optical SETI* proposes to look for coherence properties of incoming light in a way that can distinguish laser light from emission lines at the atomic level. This experiment proposal suggests that a better way to determine this is to use an approach with the sensitivity of detection available for measurements with continuous laser sources, rather than the spectroscopic measurement approach used today. Benton concludes that this method would have a better sensitivity and prevent the detection of atomic emission lines that could be mistaken for laser emissions[26].

Benton's proposal includes many figures that display frequency, signal detection, and schematics for interferometers. He also includes the equations used for his calculations determining how the process would work and be improved. His paper is well organized and discusses the effectiveness and issues regarding his alternative methods for determining the number of photons emitted from lasers. However, the issues with this method are many, and could therefore render the entire process inoperable if the ideal circumstances are not met. To counter this, Benton provides ways to combat these

problems and lists many instruments that could be used to provide additional information and support. He provides an analysis of all the figures and tables used in this article, which can allow the reader to fully understand the importance of the data[26].

This source provides a possibility on how to measure the emission of an alexandrite laser. While this article is hypothetical, it provides a baseline for how to set up an experiment and what issues should be expected to encounter along the way. This gives additional information on how the linear process can be measured and therefore gives an insight into how the nonlinear process can be observed in a way that is recordable and safe.

Objective

The objective of this research is to determine whether or not a nonlinear multiphoton effect is present in alexandrite. The methods were determined through analysis of previous experiments of a similar nature and experimental work laying out a laser optic experiment that would be most suitable for the desired effect to be detected. Based on prior measurements in the similar Cr^{3+} ion system of ruby, it is expected that a nonlinear, multiphoton effect will be present in alexandrite.

Methods

Safety Precautions

The laser used for this experiment was a Coherent Chameleon Vision-S titanium-sapphire laser (Figure 4). This laser provides tunable pulses from 690 nm to 1050 nm, or from red to near-infrared. It can provide 80 million pulses per second with a pulse energy of approximately 50 nJ per pulse. Because this laser used is deemed a category IV laser by the FDA[27], certain precautions must be put into place in order to ensure the safety of the personnel involved and the integrity of the components used. These safety precautions involved terminating all stray beams that may form from reflections off the optical components, ensuring that the no jewelry be worn anywhere on the body where it may come in contact with the laser, maintaining eye protection through use of goggles and keeping the eyes out of the plane of the laser, and other methods[28].

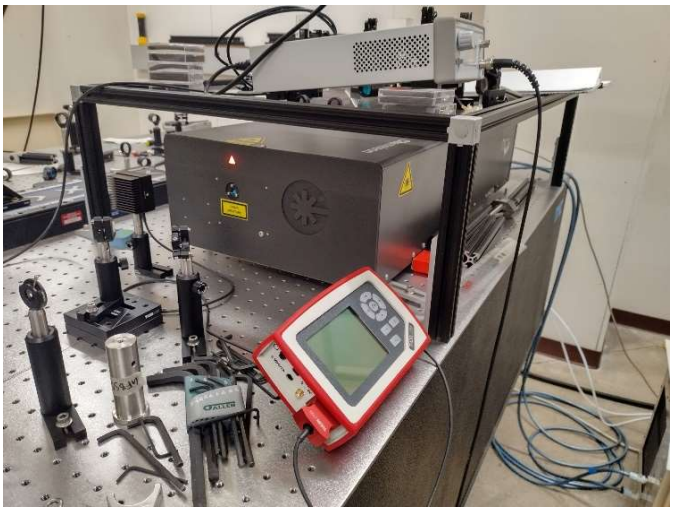

Figure 4: Coherent Chameleon Vision-S titanium-sapphire laser used in the lab setting.

Initial Experiment Setup

The first experiment setup was done in a similar manner to previous experiments performed with ruby using the same laser[17]. As this was a known method that provided strongly suggestive results, a similar alignment of the optical components was performed

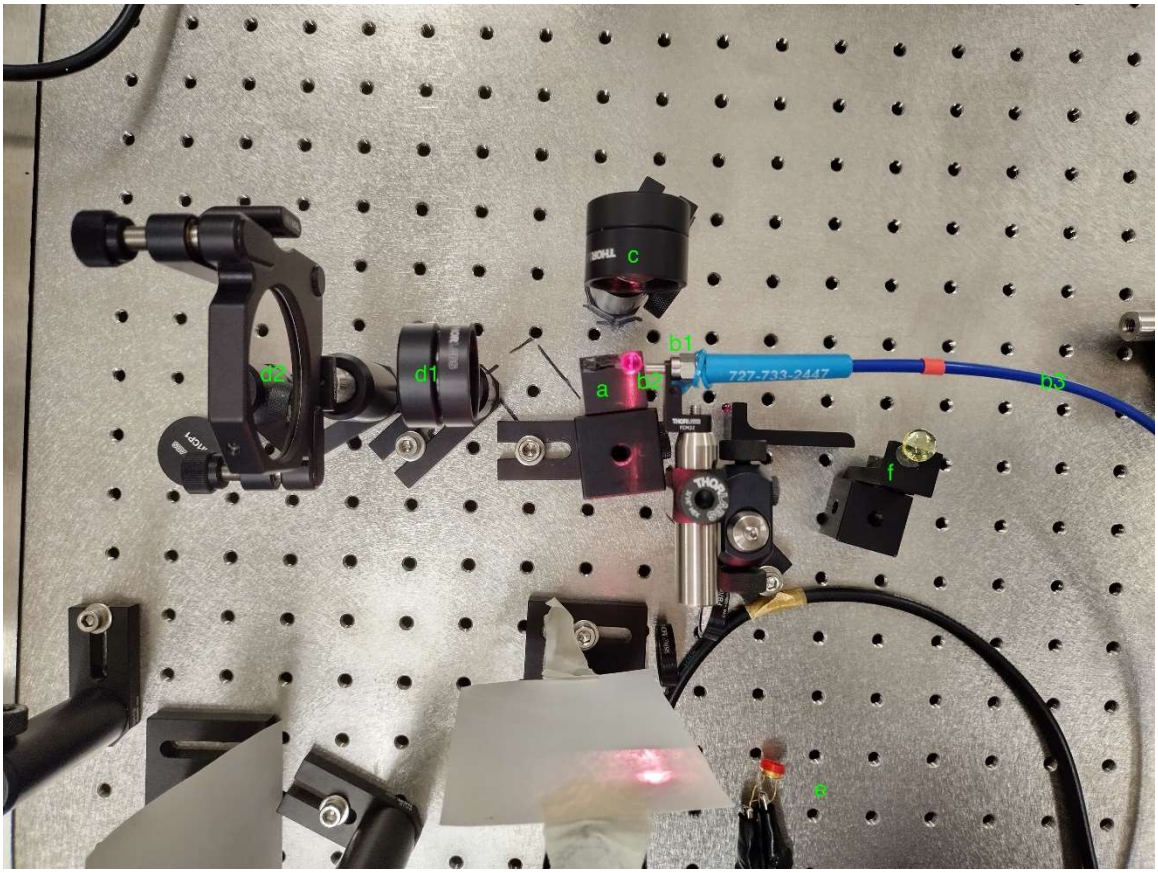

Figure 5: Initial Setup of Alexandrite Excitation Experiment with (a) Alexandrite Crystal, with Visible Fluorescence from a Columnar Region, (bX) Elements of Optical Fiber Connected to USB Spectrometer, (b1) Metal Ferrule of Optical Fiber, (b2) Optical Fiber Tip, (b3) Soft Plastic Jacket for Optical Fiber, (c) Focusing Lens; (dX) Additional Optical Elements, (d1) Collimating Lens and (d2) Retroreflector 2" Mirror, (e) Photodiode, Out of its Mount, (f) Uranium Glass Bead

for the alexandrite sample. This included the mounting of a half-sphere sample of alexandrite to an optic stand using clear glue. The glue was placed only on the lower portion of the sample so as to not absorb any laser light or interfere with the fluorescence of the alexandrite. The laser was tuned to a visible wavelength in order to align the direction of the excitation beam using several optical mirrors and irises, steering the laser towards the sample at a location where other components on the board were mostly undisturbed.. The beam was directed with the final optical mirror towards a convex lens (Figure 5, c), which

focused the light to a point onto the sample (Figure 5, a). The interaction of the laser with the Cr^{3+} chromophores within the alexandrite caused fluorescence emission in all directions, some of which was collected with an optic fiber tip (Figure 5, b2). In order to potentially collect more of the desired signal, a second convex lens (Figure 5, d1) was placed near the sample at the focal point of the lens followed by a mirror (Figure 5, d2). This would cause any fluorescence from the alexandrite to be columnated through the lens, reflected from the mirror, and focused through the lens to be sent back through the alexandrite and into the optic fiber. The signal was then carried through the plastic-coated fiber (Figure 5, b3) connected to the optic fiber tip via the metal ferrule (Figure 5, b1) to a USB spectrophotometer. The wavelength of the laser was tuned to several values, including 740 nm, 800 nm, and 840 nm where data was recorded, and the spectrometer's collection time, which is commonly called the integration time, since the spectrometer integrates the signal during this time period, was adjusted to provide a readable graph on the spectrophotometer.

Note: Also pictured above are a photodiode (Figure 5, e) and a mounted bead of uranium glass (Figure 5, f) that were not used in this portion of the experiment.

Adjusted Experiment Setup

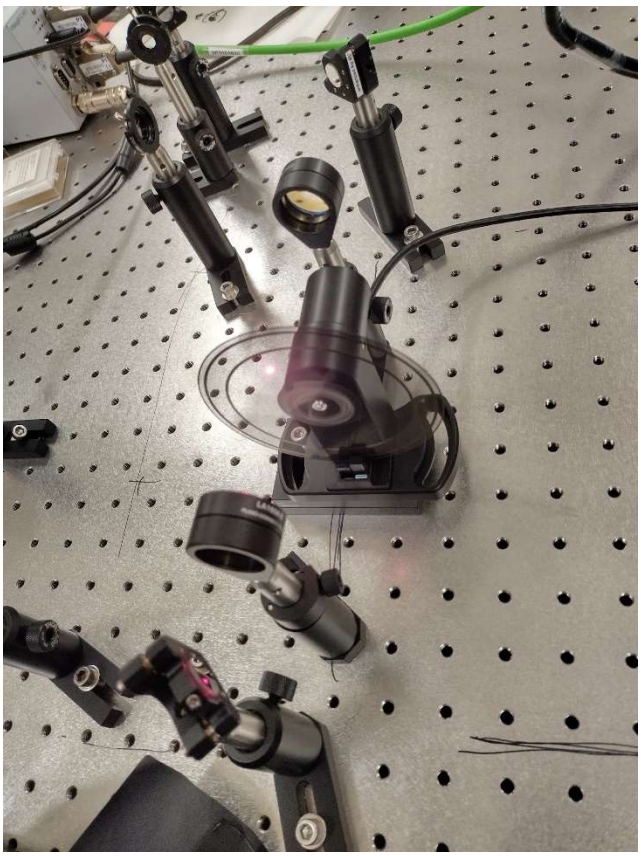

Figure 6: An optical chopper wheel placed at the focus of a Keplerian telescope in the Laser Path for the Second Laser Setup

Due to very weak signals being detected in the initial setup, the placement of the optical components was adjusted in order to characterize emission signals using a photodiode and an oscilloscope. Lock-in detection was used to study the weak fluorescence signal measured with a photodiode, which was superimposed on the background that contained too much noise for easy interpretation. In order to obtain these signals, an optical chopper paired with a Keplerian telescope (Figure 6) was placed near the start of the laser path. The optical chopper spun rapidly to briefly block the laser beam from passing through to the rest of the established path, preventing the light from striking the sample for very short intervals of time. The Keplerian telescope was used to narrow the beam, allowing for a faster cut-off and resumption of the laser. The faster this cut-off occurs and the faster the light returns to the sample, the less ambiguous the detected signal will be, and the more accurately the background can be measured and factored out of the resulting measurements by the lock-in amplifier. After passing through the optical chopper, the beam was reflected with an optical mirror towards the modified setup (Figure 7). The beam passed through a neutral density filter stand (Figure 7, a), which held various neutral density filters at different

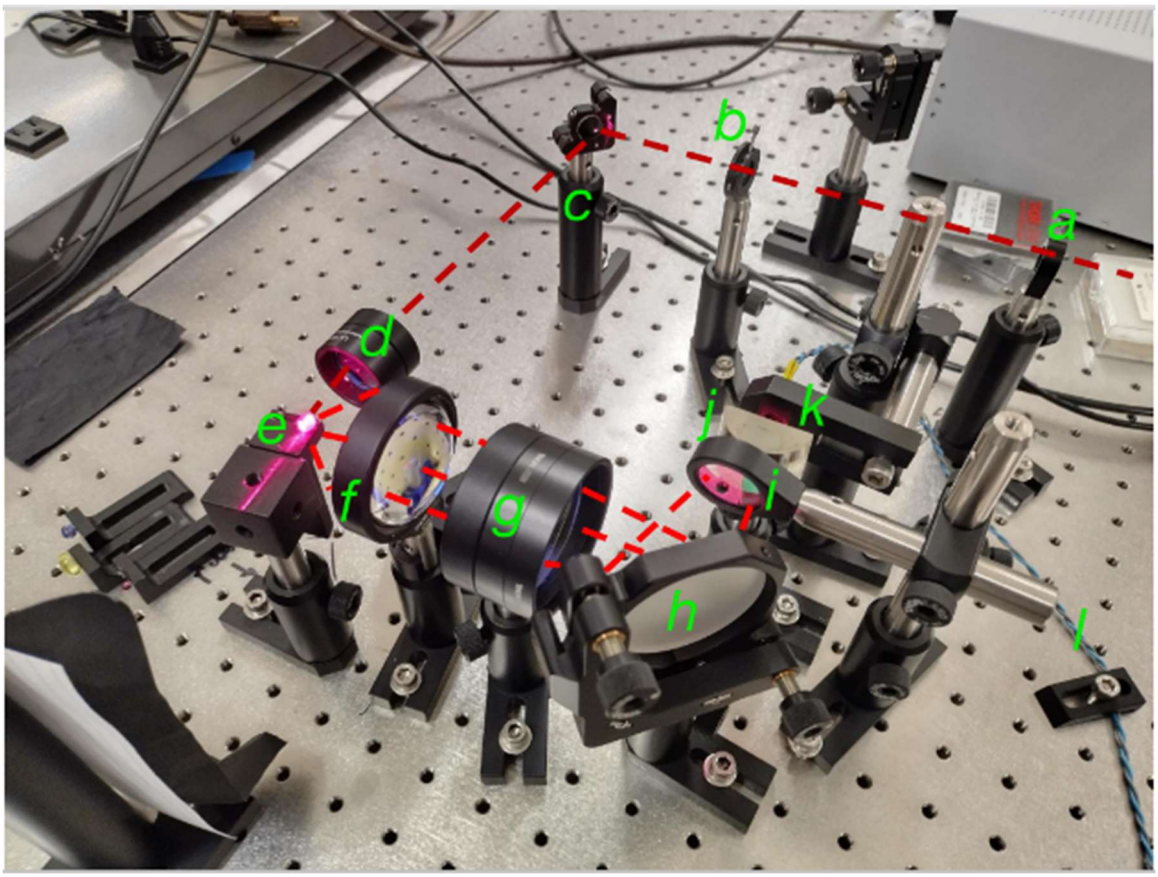

Figure 7: Experiment to Measure Fluorescence from a Two-Photon Absorption in Alexandrite with (a) a Holder for Neutral Density Filters, (b) an Iris Used to Align the Laser, (c) a Turning Mirror Used to Steer the Excitation Beam Onto the Sample, (d) Focusing Lens – 1" Focal Length, 1" Diameter Lens, (e) Cabochon Cut Alexandrite Sample, (f) Collection Optic, (g) Focusing Lens, (h) Turning Mirror, (i) Filter to Block Scattered Light from the Excitation Laser Beam while Passing the Fluorescence Emission from the Alexandrite, (j) Cylindrical Lens, (k) Photodiode, and (l) Twisted Pair Wires from Photodiode to Lock-In Amplifier and Oscilloscope.

optical density values. These filters reduce the power of light regardless of wavelength and can be stacked to result in differing values of light reduction. The beam then passed through an iris (Figure 7, b) and reflected off an optical mirror (Figure 7, c) towards a convex lens (Figure 7, d). This lens focused the light to a point onto the alexandrite sample (Figure 7, e) which then fluoresced in all directions. Two 30 mm focal length lenses in contact with each other (Figure 7, f) were placed close to the alexandrite to ensure as much collection of the resulting light as possible. This combination of two lenses was done to shorten the collective focal length of the lens system, collimating the emitted light, which was then focused using another convex lens (Figure 7, g). A large optical mirror (Figure 7, h) turned

the now focusing light towards a 700 nm wavelength filter (Figure 7, i). This filter blocked out any scattered light from the excitation beam that may have reflected off any optical components, while still allowing for an observation of the shorter wavelength fluorescence emitted by the alexandrite after the nonlinear multiphoton effect. The light then passed through a half-cylindrical lens (Figure 7, j). This lens allowed for the light to be focused to a single point, as the emission light resulted in a line due to the excitation beam entering the sample in a line. Because the photodiode can only detect a single spot of light, this lens ensured that all the available power at the relevant emission wavelengths were able to be measured by the photodiode (Figure 7, k). This signal was then sent to the lock-in amplifier and oscilloscope via the connected wires (Figure 7, l) that were twisted together and mounted to the table to prevent movement. The wavelength of the laser was tuned to a wavelength where both off-resonant single-photon and multi-photon absorption could occur, 800 nm, and neutral density filters screwed into the stand at random and repeated values. Using random and repeated values allows for a counter to any power fluctuations that may occur within the laser itself. The optical density factor of these filters were recorded, providing data for the Relative Input Power of the excitation laser, and the resulting fluorescence intensity value collected from the lock-in amplifier for each was recorded as Alexandrite Fluorescence Emission.

Results and Discussion

Initial Experiment

The results gathered from the first experiment were displayed as intensity as a function of wavelength. These measurements were taken using the optical fiber connected to a USB spectrophotometer and the graphs optimized for better interpretation.

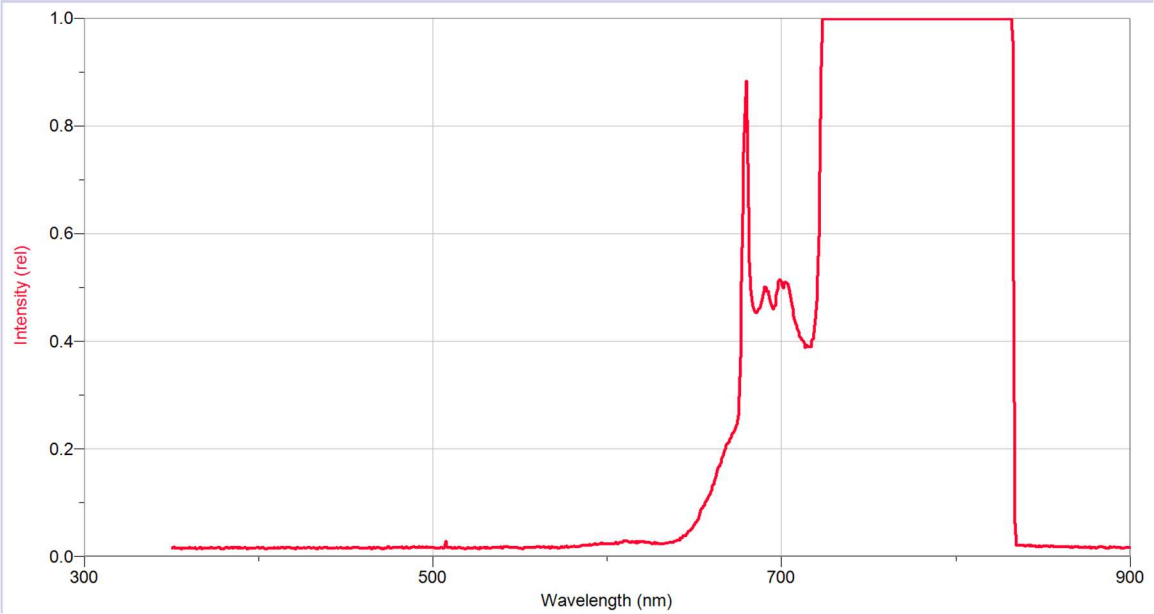

Figure 8: Intensity as a Function of Wavelength for 740 nm Wavelength Alexandrite Excitation - 250 ms Collection

For the first graph taken (Figure 8), the wavelength of the laser was set to 740 nm and the software set to 250 ms collection. Many peaks are visible, the most notable being a sharp peak around 680 nm and a broad peak ranging from approximately 730 nm to 840 nm. A very small peak is also visible around 510 nm, and slight background noise is present.

The second graph taken (Figure 9) had the laser set to 800 nm and the software set to 500 ms collection. Peaks are visible around 680 nm, 710 nm, and a broad peak ranging from 730 nm to 840 nm. There is also another small peak located at 510 nm and an increase in background noise.

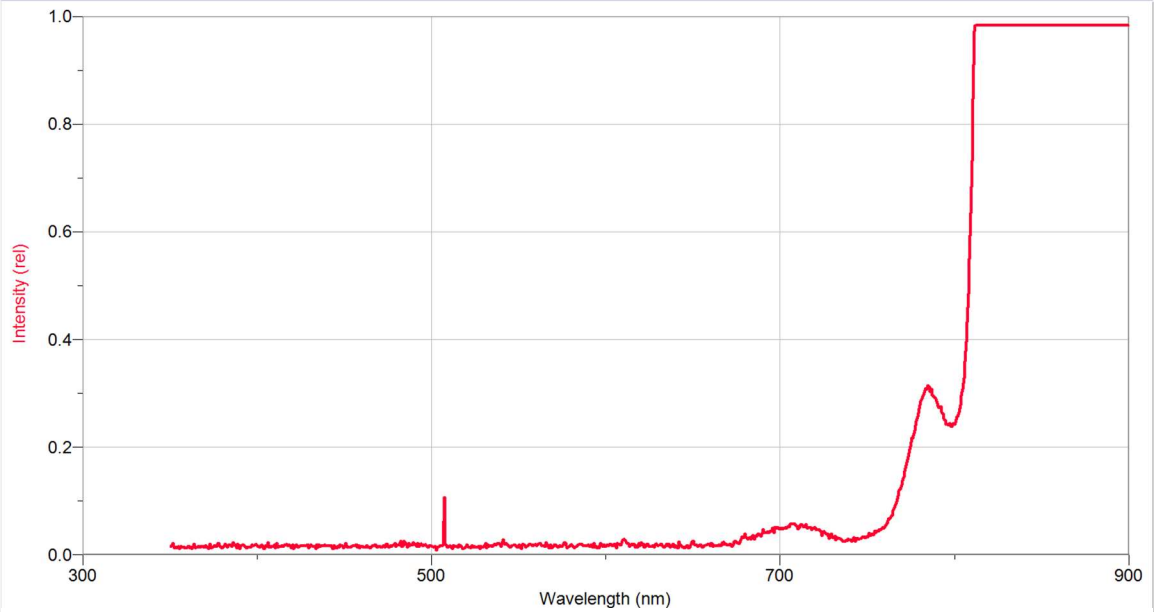

Figure 10: Intensity as a Function of Wavelength for 800 nm Wavelength Alexandrite Excitation - 500 ms Collection

The third graph taken (Figure C) had the laser set to 840 nm and the software set to 1000 ms collection. Peaks are visible around 780 nm and a broad peak at about 820 nm and above, as it goes off the end of the graph. The peak around 510 nm is still present, and more background noise is visible. The peak of interest located around 680 nm is barely

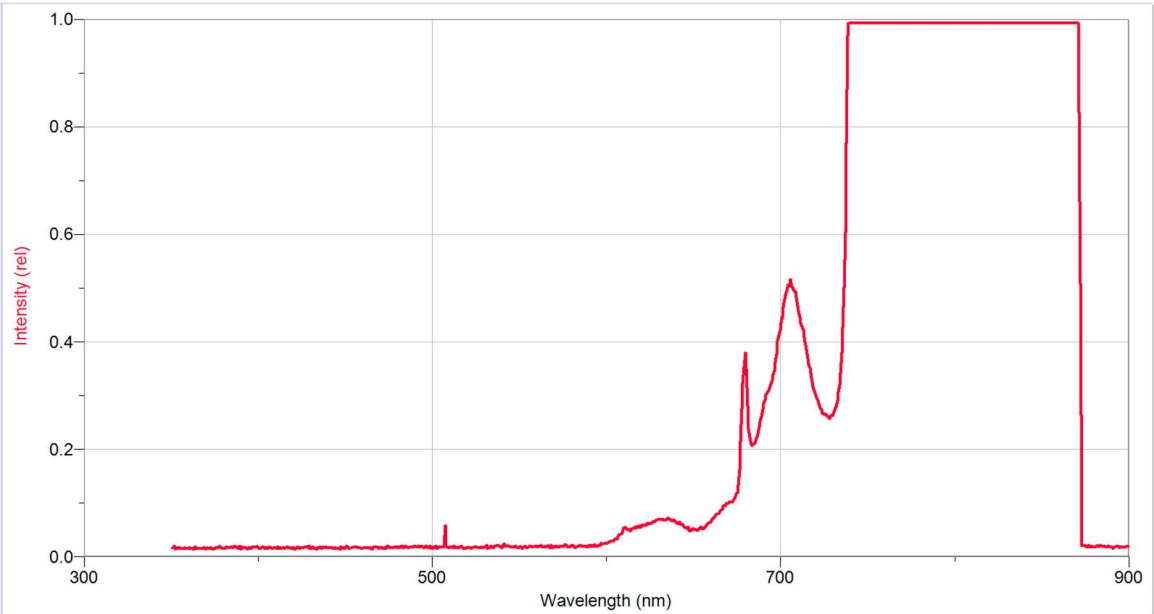

Figure 9: Intensity as a Function of Wavelength for 840 nm Wavelength Alexandrite Excitation - 1000 ms Collection

noticeable due to the background noise increasing significantly, which now overwhelms the weak emission at 680 nm.

Interpretation of Initial Results

While tuning the laser to change the photon energy, a consistent peak located around 680 nm suggested the presence of a nonlinear multiphoton effect – intuitively, it should be impossible for lower energy photons in the near-infrared laser to directly excite this higher energy transition at 690nm, but it was possible that photons in the high-energy, lower wavelength tail of the laser's spectrum had sufficient energy to drive a far off resonance single photon absorption. However, as the laser was tuned to a more desirable wavelength where the laser spectrum would no longer overlap with any of the alexandrite emission features and where the laser's highest energy photons would lack sufficient energy to excite single-photon transitions, the peak of interest at 680 nm decreased significantly in intensity. The large broad peak that was present around the 800 nm wavelength area was determined to be the laser emission affecting the optic fiber tip. The peak located around 510 nm was determined to be from the orange safety light present on the laser itself. This was determined by covering said safety light with a piece of black foil and observing the disappearance of the peak. The presence of background noise prevented the observation of the desired outcome at the laser tuned to 840 nm wavelength, and therefore a different method of testing was required.

Modified Experiment

Quantitative data from the modified experiment were collected with the use of a photodiode connected to a lock-in amplifier. The effect of the background noise was eliminated using the lock-in with an optical chopper, and the data graphed as alexandrite fluorescence emission as a function of incident excitation power. The value produced by the lock-in amplifier was used as the alexandrite fluorescence emission, and the total number value of the neutral density filters used was used to determine the relative incident excitation power.

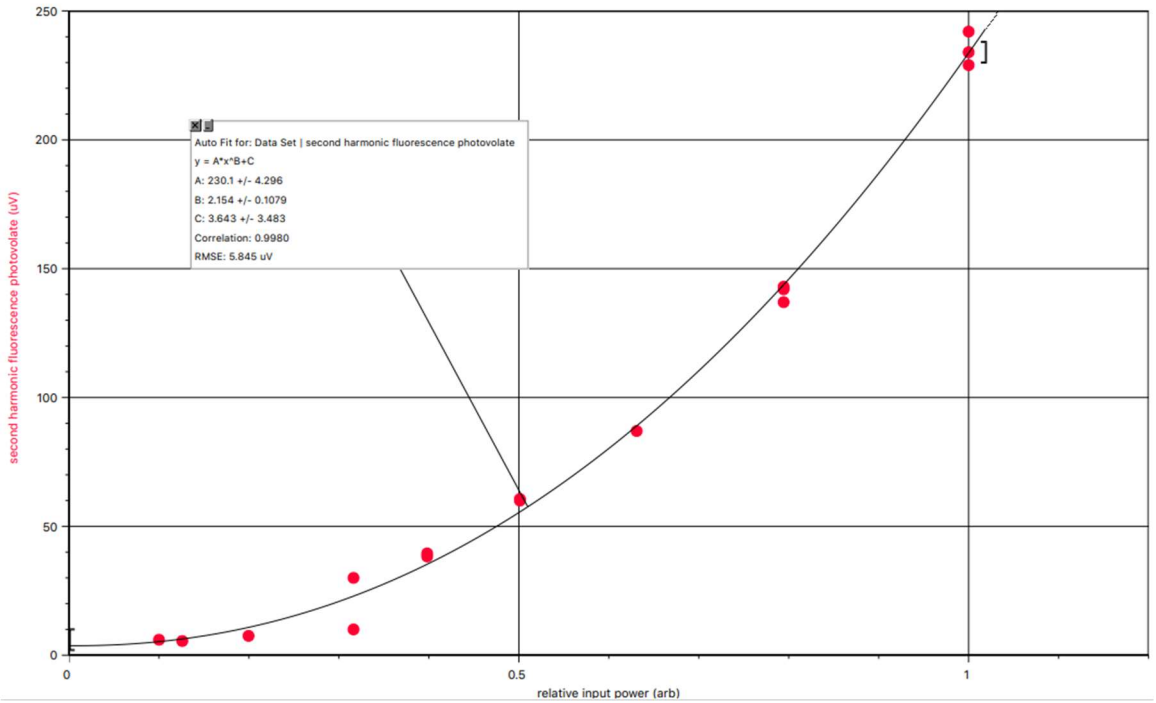

Figure 11: Second Harmonic Fluorescence Photovolate as a Function of Relative Input Power at 800 nm Wavelength Excitation

For the first set of results gathered (Figure 11), the laser was tuned to 800 nm and varying neutral density filters stacked and screwed into the stand in a random order with repeated measurements for each given value of neutral density. The resulting graph clearly shows the slope to be quadratic.

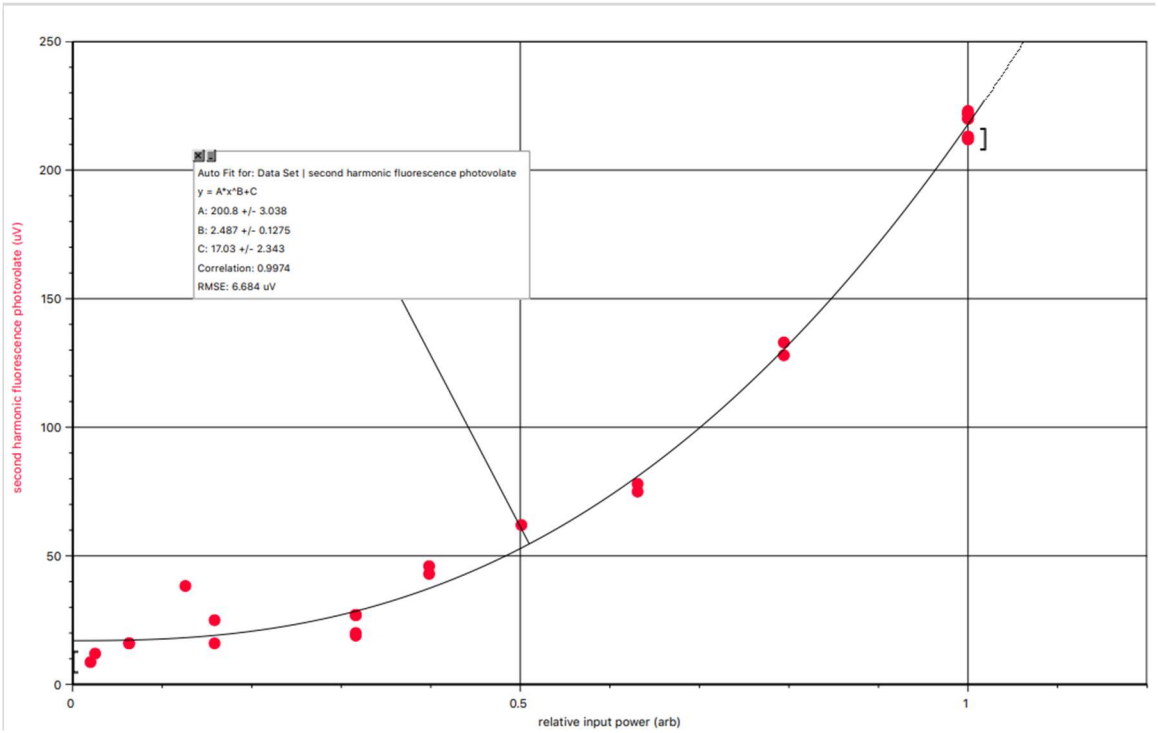

Figure 12: Second Harmonic Fluorescence Photovolate as a Function of Relative Input Power at 800 nm Wavelength Excitation

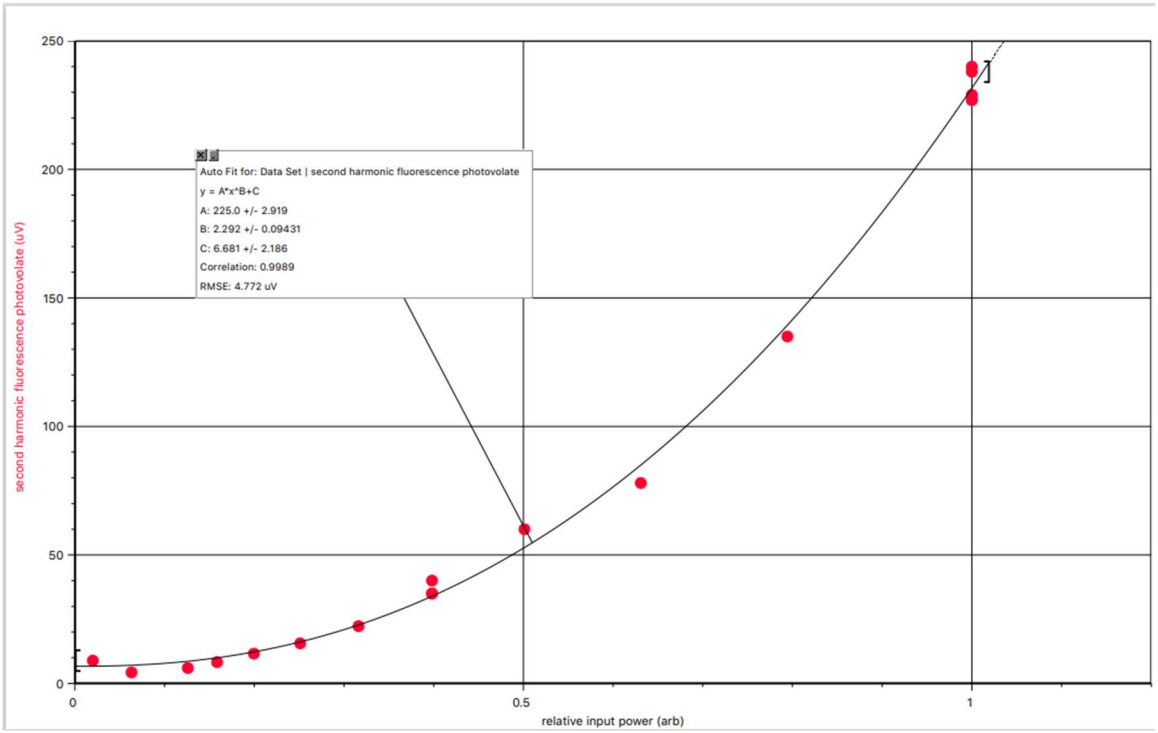

Figure 13: Second Harmonic Fluorescence Photovolate as a Function of Relative Input Power at 855 nm Wavelength Excitation

The second set of results (Figure 12) was taken with the laser tuned to 850 nm and

various neutral density filters screwed in at random and repeated intervals. The resulting graph was also shown to be quadratic.

The final results (Figure 13) were taken with the laser tuned to 855 nm, following the established procedure for the neutral density filters. The resulting graph was shown to be quadratic.

Interpretation of Secondary Results

The presence of a quadratic slope is a definitive indicator that a nonlinear multiphoton effect is present in the selected wavelength range. The absence of the background for this portion of the experiment allowed for a more accurate reading of the relevant information, and the 855 nm wavelength that the laser was tuned to should have little to no presence of a linear single-photon effect. Therefore, based on these results, it can be determined that a nonlinear multiphoton effect is present within alexandrite. The correlation of the graphs generated by the software was over 0.99, therefore indicating that the line of best fit has a high correlation to the data points and can be accepted as an accurate representation of the data. Were the light incident on the photodiode due to emission after single-photon absorption or due to scattering of the laser in the experiment (even with the spectral filter, a small amount of scattered light will inevitably reach the detector), the data shown here would have a linear functional dependence on intensity. Our result, then, is a definitive measurement of a two-photon process.

Conclusions

In conclusion, this experiment was able to find definitive evidence that a nonlinear multiphoton effect occurs in alexandrite, which can be easily measured using ultrafast laser pulses. Through the use of many literature reviews and hands-on experimental work, the methods of testing were able to be determined and were deemed effective. While some experimental issues were encountered along the way, such as the placement of the optical components on the board, suppression of stray beams, and detection of weak signals copropagating with strong background noise, these complications were corrected so that they would not influence the results.

Future Research

Because the results from the alexandrite testing displayed conclusive evidence of a nonlinear multiphoton effect, it can be assumed that the components used were effective at testing the presence of this occurrence within a material. While other research currently exists of the presence of this phenomenon in ruby, future research could include the potential observance of this effect in other materials containing a Cr^{3+} ion chromophore. This would include emerald and chromium-doped glass. Because it is known that the Cr^{3+} ion has the capability to experience a nonlinear multiphoton effect, this expanded research would observe how the chromophore functions in different matrices. We have considered looking at aqueous solutions of Cr^{3+} ions to determine if a similar effect can be observed in the liquid phase, but have delayed this investigation due to the highly toxic nature of chromium (iii) nitrate.

Further research could include the examination of uranium glass, henna, and chlorophyll-A in this experiment setup as well. While uranium glass does not contain a

Cr^{3+} ion, it contains a U^{4+} ion that may hold the potential to undergo a nonlinear multiphoton effect. The investigation of henna is another potential experiment, because it contains a 1,4-napthoquinone[29] chromophore that has been subject to minimal spectroscopic study. Chlorophyll-A has been studied in the past for this kind of observation[30], but only in the context of more complicated spectroscopic measurements, rather than a straightforward two-photon characterization such as the one performed in this experiment. Future testing of this phenomenon in materials not containing chromium could provide insight into how the nonlinear multiphoton process works with a larger variety of chromophores.

Bibliography

(1) GIA & Tino Hammid, courtesy Mayer & Watt. While Russia Is the Most Famous Alexandrite Source, This Stone from Brazil Shows Beautiful Color Change from Daylight (Left) to Incandescent Light (Right). https://www.gia.edu/alexandrite-quality-factor.

(2) Gübelin, E.; Schmetzer, K. Gemstones with Alexandrite Effect. In Gems & Gemology; Liddicoat, R., Keller, P., Manson, D., Koivula, J., Keller, A., Fryer, J., Thomas, S., Fryer, C., Dirlam, D., Ross, M., Dillion, S., Eds.; Gemological Institute of America, 1982; Vol. 18.

(3) Li, M.; Bai, Y.; Duan, Z.; Yuan, R.; Liu, X.; Liu, Y.; Liang, X.; Wu, H.; Zhuo, F. Efficacy and Safety of Long-Pulsed 755-Nm Alexandrite Laser for Keratosis Pilaris: A Split-Body Randomized Clinical Trial. Dermatology and Therapy 2022, 12 (8), 1897–1906. https://doi.org/10.1007/s13555-022-00771-5.

(4) Hecht, J. History of Gas Lasers Part 1—Continuous Wave Gas Lasers; OPN Optics & Photonics News, 2010; pp. 16–23.

(5) Denker, B.; Shklovsky, E. Handbook of Solid-State Lasers: Materials, Systems, and Applications; Woodhead Publishing Limited, 2013.

(6) Coldren, L. A.; Corzine, S. W.; Mashanovitch, M. L. Diode Lasers and Photonic Integrated Circuits; John Wiley & Sons, 2012.

(7) Haedersdal, M.; Wulf, H. Evidence-Based Review of Hair Removal Using Lasers and Light Sources. Journal of the European Academy of Dermatology and Venereology 2006, 20 (1), 9–20. https://doi.org/10.1111/j.1468-3083.2005.01327.x.

(8) Saedi, N.; Metelitsa, A.; Petrell, K.; Arndt, K. A.; Dover, J. S. Treatment of Tattoos with a Picosecond Alexandrite Laser. Archives of Dermatology 2012, 148 (12), 1360. https://doi.org/10.1001/archdermatol.2012.2894.

(9) Khemasuwan, D.; Mehta, A. C.; Wang, K.-P. Past, Present, and Future of Endobronchial Laser Photoresection. Journal of Thoracic Disease 2015, 7 (Suppl 4), S380–S388. https://doi.org/10.3978/j.issn.2072-1439.2015.12.55.

(10) Forman, P. Inventing the Maser in Postwar America. Osiris 1992, 7 (1), 105–134. https://doi.org/10.1086/368707.

(11) Maiman, T. H. Stimulated Optical Radiation in Ruby. Nature 1960, 187 (4736), 493–494. https://doi.org/10.1038/187493a0.

(12) Göppert-Mayer, M. Elementary Processes with Two Quantum Transitions. Annalen der Physik 2009, 18 (7-8), 466–479. https://doi.org/10.1002/andp.200910358.

(13) Campbell, M. The Institute of Optics and the Laboratory for Laser Energetics: A Dynamic Duo. In A Jewel in the Crown II: Essays in Honor of the 90th Anniversary of the Institute of Optics University of Rochester; Stroud, Ed.; Kern, Translator.

(14) Kleinman, D. A. Laser and Two-Photon Processes. Physical Review 1962, 125 (1), 87–88. https://doi.org/10.1103/physrev.125.87.

(15) Kaiser, W.; Garrett, C. G. B. Two-Photon Excitation in CaF2:Eu2+. Physical Review Letters 1961, 7 (6), 229–231. https://doi.org/10.1103/physrevlett.7.229.

(16) Abella, I. D. Optical Double-Photon Absorption in Cesium Vapor. Phys. Rev. Lett. 1962, 9 (11), 453–455. https://doi.org/10.1103/physrevlett.9.453.

(17) Hardin, W. D.; Mills, Jon. T.; Stuart, J. M.; Sulfridge, E. B.; Tanner, T. A.; Jarvis, T. W. Femtosecond Excitation of Two-Photon Absorption in Ruby. Spectroscopy Letters 2022, 1–14. https://doi.org/10.1080/00387010.2022.2123000.

(18) Morgenshtern, Z. L.; Neustruev, V. B. Phosphorescence and Band Structure of Ruby. Sov. J. Exp. Theor. Phys. Lett. 1965, 2, 316-318.

(19) Morgenshtern, Z. L.; Neustruev, V. B. Two-Stage Excitation of the Phosphorescence of Ruby. Phys. Status Solidi B 1966, 14 (2), 303–310. https://doi.org/10.1002/pssb.19660140206.

(20) Riley, K. F.; Hobson, M. P.; Bence, S. J. Mathematical Methods for Physics and Engineering; Cambridge University Press, 2006.

(21) Hecht, J. How the Laser Launched Nonlinear Optics. Optics and Photonics News 2010, 21 (11), 34. https://doi.org/10.1364/opn.21.11.000034.

(22) Dalzell, C. J.; Han, T.P.; Ruddock, I. S. The two-photon absorption cross-section of ruby and distributed crystal fibre sensing." In SPIE 20th. Int. Conf. Opt. Fibre Sens. 2009, 7503: 947-950. https://doi.org/10.1117/12.835101.

(23) Göppert, M. Über Die Wahrscheinlichkeit Des Zusammenwirkens Zweier Lichtquanten in Einem Elementarakt. Naturwissenschaften 1929, 17, 932–932. https://doi.org/10.1007/BF01506585.

(24) Serway, R. A.; W, J. Physics for Scientists and Engineers with Modern Physics; Cengage: Australia, 2019.

(25) Thornton, S. T. Modern Physics for Scientists and Engineers.; Cengage, 2019.

(26) Benton, D. M. A Proposed Method for a Photon-Counting Laser Coherence Detection System to Complement Optical SETI. Publications of the Astronomical

Society of the Pacific 2019, 131 (1001), 074501. https://doi.org/10.1088/1538-3873/ab1a46.

(27) Center for Devices and Radiological Health. Laser Products and Instruments. U.S. Food and Drug Administration. https://www.fda.gov/radiation-emitting-products/home-business-and-entertainment-products/laser-products-and-instruments.

(28) Jarvis, T. Laser Safety Training, 2022.

(29) Amada, I.; Yamaji, M.; Tsunoda, S.; Shizuka, H. Laser Photolysis Studies of Electron Transfer between Triplet Naphthoquinones and Amines. Journal of Photochemistry and Photobiology A: Chemistry 1996, 95.

(30) Šebelík, V.; Kuznetsova, V.; Lokstein, H.; Polívka, T. Transient Absorption of Chlorophylls and Carotenoids after Two-Photon Excitation of LHCII. The Journal of Physical Chemistry Letters 2021, 12 (12), 3176–3181. https://doi.org/10.1021/acs.jpclett.1c00122.