MID – INFRARED SOLID STATE LASERS
FOR SPECTROSCOPIC APPLICATIONS

by

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MID – INFRARED SOLID STATE LASERS
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PHYSICS

ABSTRACT

This work is devoted to study of novel high power middle-infrared (Mid-IR) laser sources enabling development of portable platform for sensing of organic molecules with the use of recently discovered Quartz Enhanced Photo Acoustic Spectroscopy (QEPAS). The ability to detect small concentrations is beneficial to monitor atmosphere pollution as well for biomedical applications such as analysis of human breath to detect earlier stages of cancer or virus activities.

A QEPAS technique using a quartz tuning fork (QTF) as a detector enables a strong enhancement of measured signal when pump laser is modulated with a frequency coinciding with a natural frequency of a QTF. It is known that the detectability of acousto-optics based sensors is proportional to the square root of the laser intensity used for detection of analyte. That is the reason why commercially available semiconductor Mid-IR lasers having small output power limit sensitivity of modern QEPAS based sensors. The lack of high power broadly tunable lasers operating with a modulation frequency of quartz forks (~ 32.768 kHz) is the major motivation of this study.

Commercially available Mid-IR (2-3.3 µm), single frequency, continuous wave (CW) fiber pumped lasers based on transition metal doped chalcogenides (e.g. Cr:ZnSe)
prove to be efficient laser sources for organic molecules detection. However, their direct modulation is limited to several kHz, and cannot be directly used in combination with QEPAS. Hence, one objective of this work is to study and develop fiber laser pumped Ho:YAG (Er:YAG)/Cr:ZnSe tandem laser system/s. Ho (Holmium) and/or Er (Erbium) ions having long radiation lifetime (~ 10 ms) can effectively accumulate population inversion under CW fiber laser excitation. Utilization of acousto-optic (AO) modulators in the cavity of Ho:YAG (Er:YAG) laser will enable effective Q-Switching with repetition rate easily reaching the resonance frequency of a QTF. It is expected that utilization of Ho:YAG (Er:YAG)/Cr:ZnSe tandem will further result in effective conversion of monochromatic radiation of Ho/Er lasers in a broadly tunable Mid-IR radiation compatible with QEPAS detection.

**Keywords:** lasers; solid state; mid-infrared; q-switching; single frequency; spectroscopy.
DEDICATION

I dedicate this work to my family who has been always inspiring me to understand the universe around.
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CHAPTER I

OVERVIEW OF SOLID STATE LASERS OPERATING IN EYE-SAFE MIDDLE-INFRARED REGION

1.1 Introduction

This study addresses the output parameters of Ho:YAG and Er:YAG lasers relevant for their use as pumping sources for Mid-IR tunable Cr^{2+}:ZnSe/Cr^{2+}:ZnS lasers. Cr^{2+}:ZnS lasers will be further integrated with QEPAS detection system to form a compact portable “Optical Nose” platform. The demonstrated platform is promising for sensing applications. A brief historical background of how lasers were discovered introduced in the next paragraph is followed by a discussion of different regimes of laser operation (e.g. CW mode, active and passive Q-switched modes, and gain-switched regime).

The following section focuses on describing the meaning of eye-safe spectral region and its importance for a variety of applications. An overview of Solid State Lasers (SSL) operating in eye-safe spectral region is presented in section 1.3. Lasers based on Tm^{3+}, Ho^{3+}, and Er^{3+} rare earth ions are discussed followed by a description of lasers based on Cr^{2+} and Fe^{2+} transition metal ions doped into chalcogenide (e.g. ZnSe and ZnS) host materials. Applications of lasers are described in section 1.4. Advantages and disadvantages are discussed with a detailed explanation of existing limitations. A quartz enhanced photo-acoustic spectroscopy technique is introduced in section 1.4.3. Nonlinear effect phenomena in Optical Parametric Oscillators (OPO) are shown in section 1.4.4.
Experimental results of the proposed research are presented and described in Chapters II-IV.

Chapter II is devoted to experiments on studying of Ho$^{3+}$:YAG and Er$^{3+}$:YAG lasers. The research procedure and results on study of thermal management in crystals and glasses are included and explained in chapter II. Design and measurements of characteristics of Single Frequency Cr$^{2+}$ doped ZnSe Broadband CW and Gain-Switched Lasers with Fine Tuning are presented in chapter III. Integration of a laser described in chapter III with detection system – so-called - “Optical Nose” platform is presented in chapter IV. Results of the measurements of NH$_3$ molecules concentration with the use of “Optical Nose” platform are outlined at the end of the chapter IV. Conclusions and future work are summarized in chapter V. A list of literature this paper refers to is outlined in the last section.

1.2 Background

1.2.1 History of a Lasers

An over a century ago in 1898 a science fiction novel by H. G. Wells (The Time Machine, The Invisible Man) was published. The fantasy story introduces an alien invaders having weapon producing “Heat-Ray” to fight human kind. The science fiction of the late 19th century is today’s scientific reality.

The main concept of stimulated emission of radiation, on which lasers are based on, was introduced [1] for the first time in 1916 by A. Einstein. A decade later, in 1928, Rudolf W. Ladenburg confirmed [2] the existences of the phenomena of stimulated


Meanwhile, in the Soviet Union, Nikolay Basov and Aleksandr Prokhorov were independently working on the quantum oscillator and solved [6] the problem of CW (Continuous Wave) systems by introducing more than two energy levels. Such gain media could provide stimulated emissions between an upper excited state and a lower excited state, but not the ground state, simplifying utilization of a population inversion.

In 1955, Prokhorov and Basov suggested optical pumping of a multi-level system as a method for obtaining the population inversion, later a main method of laser gain media excitation. By 1960, Theodore H. Maiman had constructed the first functioning laser [7]. Maiman’s laser used a solid-state flashlamp-pumped synthetic ruby crystal ($\text{Cr}^{3+}:\text{Al}_2\text{O}_3$) producing red laser light at 694 nanometers wavelength. In 1964 Charles H. Townes, Nikolay Basov, and Aleksandr Prokhorov shared the Nobel Prize in Physics, “for fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser–laser principle” [8].
1.2.2 Regimes of Operation

1.2.2.1 CW Mode

Lasers can operate in continuous or pulsed regimes. Those ones with constant output power over time named CW (continuous wave) lasers. Lasers operating in other than CW regime named pulsed or pulse-periodic lasers. Pulsed lasers feature some pulse duration and pulse repetition rate.

1.2.2.2 Q-Switching.

Pulse repetition rate is a convenient mode of laser operation when it is necessary to have a trace of output pulses. Simply it could be achieved by modulating of either pumping source (pulsed pumping) or output power of the laser itself. A mechanism of switching a quality factor of the resonator rather than modulating pumping power named Q-switching is used to produce high energy pulses with a short duration. Quality factor is a ratio of the energy stored in an oscillating system to that one loosing within one period. The method of giant pulse formation by switching quality factor of the laser resonator was first proposed [9] in 1958 by Gordon Gould. Q-switching differentiates on active Q-switching and passive Q-switching.
1.2.2.2.1 Active Q-Switching. In case of active Q-switching an active element is used to switch the quality factor by incorporating losses in a laser resonator. This will allow the inversion population to build up and store more energy in the cavity. When the losses are removed rapidly the laser pulse of a high power formed releasing stored energy from the gain media within few round trips of the laser resonator. The simplest active Q-Switch is a chopper. However the best characteristics such as stability and frequency range are obtained with the use electro-optical (EO) and acousto-optical (AO) Q-switch crystals. The first demonstration of the active Q-Switching was realized by R.W. Hellwarth and F.J. McClung using electro-optical Kerr cell in a cavity of the ruby laser [10].

1.2.2.2 Passive Q-Switching. When the high peak power is important the simple and inexpensive design of Q-switching involves so-called passive Q-Switches or saturable absorbers. During the pumping the energy is storing in a resonator (without lasing due to high intracavity losses) and partially absorbed by passive Q-switch saturable absorber. At one point passive Q-Switch starts to saturate and quickly becomes transparent, dramatically decreasing cavity losses. This process is accompanied by a giant pulse formation. The first demonstration [11] of the passive Q-Switching using liquid saturable absorber was done in 1964 with the ruby laser.

1.2.2.3 Gain-Switching. Gain switching is a method for laser pulse formation by modulating the laser gain via the pumping power. The term gain-switching originates from the fact that the optical gain is negative when population inversion is below threshold, and switches to a positive value when population inversion exceeds the cavity threshold. Thus, the first laser designed was based on optically pumped ruby crystal and
operated in gain-switched mode. An output laser pulse forms with a certain delay with respect to a flash lamp pumping pulse duration because it takes a few resonator round trips for it to build up from a spontaneous emission.

1.2.3 Eye-Safe Spectral Region

Absorption and penetration depth in water and other biological tissues for different wavelengths are depicted in Figure 1 [12]. One can see that wavelengths above 1.4 μm are strongly absorbed by water. Water contained in cornea and the vitreous part of the eye absorb laser light with a wavelength longer than 1.4 μm within a few hundreds of microns preventing it reaching the retina.

Note: From “2 μm Laser Sources and Their Possible Applications” by Karsten Scholle, Samir Lamrini, Philipp Koopmann and Peter Fuhrberg, 2010, Frontiers in Guided Wave Optics and Optoelectronics, p. 471. Copyright 2004 by the LISA laser products OHG. Adapted with permission.

Figure 1. Absorption and penetration depth in water and other biological tissue constituents for different wavelengths

Due to the strong absorption in water, which is the main component of biological tissue, substantial energy dissipation occurs in the illuminated area [12]. Utilization of Mid-IR lasers as a precise surgical scalpel is accompanied with suppressed bleeding due
to blood clotting. The lasers described in this work are already widely utilized for health and beauty related applications. Moreover Mid-IR lasers overlap with the transparency window of the atmosphere, making them very well suited for lidar applications. They could be utilized for measuring the wind velocity, humidity, carbon dioxide concentration, and other pollutants in the atmosphere. Monitoring of the wind parameters and humidity is very useful for weather forecasting. Humidity and carbon dioxide measurements are important for the analysis of the “global warming” effect.

1.3 Overview of Solid State Lasers Operating in Eye-Safe Mid-Infrared Region

This section focuses on solid state lasers operating in the eye-safe Mid-Infrared region. Lasers based on bulk solid-state gain media doped with the rare-earth ions Tm$^{3+}$, Ho$^{3+}$, and Er$^{3+}$ are discussed in the first paragraph of this section followed by an overview of lasers based on chalcogenide ZnSe/ZnS host materials doped with Cr$^{2+}$ and Fe$^{2+}$transition metal ions.

1.3.1 Lasers Based on Rare Earth Ions

Solid state eye-safe lasers based on the Tm$^{3+}$, Ho$^{3+}$, and Er$^{3+}$ ions have been attracting great interest for many years. Successful lasing at room temperature (RT) from a lot of different solid state host materials has been reported. The relevant energy levels of Er$^{3+}$, Tm$^{3+}$, and Ho$^{3+}$ are depicted in Figure 2 [13], where only the two lowest electronic states are shown. Each of the electronic states is split into a number of crystal field energy levels and shown as thick bars in Figure 2.
Figure 2. Ground and lowest excited states of Er$^{3+}$, Tm$^{3+}$, and Ho$^{3+}$. The electronic states and configurations, and the typical wavelength regions of the transitions, are indicated in the figure. The width of the electronic states represents the crystal field splitting of the levels [13].

1.3.1.1  Tm$^{3+}$ Lasers

Efficient flashlamp and laser diode-pumped laser operation has been achieved on thulium ion transitions in a various host materials. Thulium doped fiber nad solid state lasers featuring flexibility and versatility are known for decades. With a diode pumping thulium fiber lasers have been designed with output powers in excess of 1 kW with outstanding stability of output characteristics such as power, beam shape, and output linewidth making them useful pumping sources for a number of the solid state lasers. A schematic diagram of thulium based laser operating at about 2 μm under 785 nm laser
diode pumping is depicted in Figure 3 [14]. The output wavelength range for the $^3F_4^{}-^3H_6^{}$ transition is 1.6 – 2 μm corresponds to the strongest absorption lines of most solid state active media making thulium fiber laser promising for direct resonant laser pumping source for fiber-bulk hybrids.

![Energy level diagram of the diode-pumped 2 μm Tm laser](image)

**Figure 3.** Energy level diagram of the diode-pumped 2 μm Tm laser

1.3.1.2 $Ho^{3+}$ Lasers

Direct resonant laser pumping of the Ho $^5I_7$ manifold, featuring high cross-section and fluorescence lifetime of 8-16 ms, results in high energy storage capability and efficient Q-switched operation of holmium lasers [15]. The commonly used Tm-laser based pumping sources offer a number of advantages due to a small quantum defect
between Tm laser radiation (1.9 µm) and Ho laser emission (2.09 µm): elimination of energy transfer (no sensitizer ion used), reduced up-conversion losses, linearity of gain versus absorbed pump intensity, reduced sensitivity of gain versus temperature, and high short-pulse extraction efficiency. Holmium lasers operating in CW and Q-Switched regimes with high output power and high pulse energy in the eyesafe two-micron spectral region are promising sources for biomedical, eyesafe lidar sensing, and range-finding applications. Also Q-Switched holmium laser radiation could be down-converted by optical parametric oscillators (OPO) based on high figure of merit ZnGeP$_2$ (ZGP) crystal [15] into broad spectrum of infrared region with a fine tuning of output wavelength. Such a device in a compact handheld design is able to scan absorption lines across a wide range of wavelength making so-called “optical-nose” beneficial for a variety of spectroscopic purposes.

1.3.1.3 \( \text{Er}^{3+} \) Lasers

Laser action on erbium transitions has been demonstrated in a variety of garnets, fluorides, and glasses. Erbium has attracted attention because of two particular wavelengths of interest around 2.9 µm, and at 1.5-1.65 µm. Both of these wavelengths are absorbed by water, which leads to interesting medical applications in the case of the 2.9 µm lasers, and to eye safe military rangefinders in the case of the shorter wavelengths. Room temperature luminescence of erbium ions in YAG crystal under 1532 nm fiber laser excitation is depicted in Figure 4. 1.54-1.65 µm lasers arise from a transition between the \( ^4I_{13/2} \) state and the \( ^4I_{15/2} \) ground state of Er$^{3+}$. Recently obtained [16] successful operation at 1.645 µm wavelength gives this laser a chance to serve as a
pumping source for broadly tunable mid-IR lasers based on \( \text{Cr}^{2+} \) doped ZnSe/ZnS crystals having strong absorption at this pumping wavelength.

![Graph showing 1%at. Er=YAG luminescence under 1532nm pumping](image)

**Figure 4.** Luminescence of Er:YAG at room temperature

### 1.3.2 Lasers Based on Transition Metal Ions

Recent progress in transition metal doped II-VI chalcogenide materials makes them the laser sources of choice when one needs a compact system with tunability over 1.9–5.1 \( \mu \text{m} \).

#### 1.3.2.1 \( \text{Cr}^{2+} \) Doped ZnSe/ZnS Lasers

Chromium doped zinc selenide and zinc sulfide active crystals proved to be effective sources of coherent radiation in 2-3.1\( \mu \text{m} \) spectral region under 1.5-2.1\( \mu \text{m} \).
excitation and can operate in non-selective as well as in dispersive cavities with a fine tuning of output radiation [17,18]. Absorption and emission cross-sections of Cr:ZnSe are depicted in Figure 5. One can see from the Figure 5 that the strongest absorption is around 1.7 µm. Effective pumping of such active medium can be realized with the use of Erbium lasers operating at 1.645 µm.

![Absorption and emission cross-sections of Cr:ZnSe](image)

**Figure 5** Absorption and emission cross-sections of Cr:ZnSe

Output powers exceeding 10 W and conversion efficiency up to 70% demonstrated [19,20] in several chromium doped semiconductors makes these materials ideal candidates for mid-IR tunable laser systems.
1.3.2.2 Fe\textsuperscript{2+} Doped ZnSe/ZnS Lasers

The first RT gain-switched lasing of Fe:ZnSe crystal at 4.4μm in a microchip configuration as well as in a nonselective cavity under 2.92μm excitation with a pulse duration of 5 ns was demonstrated in [21]. Selective cavity experiments were also performed in a Littrow mount configuration and tunable oscillation of Fe:ZnSe crystal over 3.9-4.8μm spectral range was demonstrated at RT. Maximum output energy was relatively small – of the order of several micro-Joules. Output energy and efficiency of Fe:ZnSe lasing at RT in gain switched regime was further improved in [22] where output energy reached 0.4 mJ at 4.4 μm with 20% quantum efficiency of lasing with respect to the pump energy. The output spectrum of the dispersive Fe\textsuperscript{2+}:ZnSe laser was continuously tuned in the spectral range 3.95-5.05 μm. Fe\textsuperscript{2+}:ZnSe lasers have potential to operate at room temperature over the spectral range extended to 3.7-5.1 μm.

1.4 Applications

This chapter summarizes possible practical use of the lasers described above as well as disadvantages that limit their utilization for applications described in this work. The ways to overcome those limitations are explained explicitly.

1.4.1 Advantages

1.4.1.1 Tm\textsuperscript{3+}, Ho\textsuperscript{3+}, and Er\textsuperscript{3+} Lasers

Laser radiation from rare earth ion transitions is utilized daily for decades especially for applications based on a strong absorption by water. These applications are summarized in Table 1:
Table 1 Applications of lasers based on rare earth elements

<table>
<thead>
<tr>
<th></th>
<th>Er$^{3+}$</th>
<th>Ho$^{3+}$</th>
<th>Tm$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Applications</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomedical applications – cutting, drilling, resurfacing of water containing biological materials</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Cosmetology</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Eye safe rangefinders</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Spectroscopy</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Scientific research</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Industrial uses (welding, cutting, micromachining, laser marking)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Direct resonant pumping source for solid state lasers such as Ho:YAG lasers</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Efficient Q-switch regime of operation</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Effective pumping for ZGP OPO</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Pumping source for Active Crystals</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>
1.4.1.2 Advantages of Cr\textsuperscript{2+} Doped ZnSe/ZnS Lasers

The advantages of utilizing Cr\textsuperscript{2+} Doped ZnSe/ZnS Lasers are outlined in Table 2.

| Efficient |
| Ultra-compact |
| Inexpensive |
| Room temperature operation |
| Broadband wavelength range 2-3 µm |
| Potential source for “optical nose” |

1.4.2 Disadvantages and Limitations

Compact pulsed laser systems are attractive for a wide range of applications. Among those are laser welding, cutting, micromachining, laser marking, where the quality of the pulse shape is not as important as the peak power. Lasers operating in more than one longitudinal or transverse mode provide intensity modulated output pulses as a result of mode beating. For instance, precision of range finding applications based on a time of flight measurements depends on pulse to pulse stability (jitter) as well as temporal and spectral quality of a pulse profile (i.e. like bell shape) that can provide single frequency laser \cite{1}. Sensitivity of laser spectroscopy methods also requires stability in pulse shape and pulse repetition rate to detect small concentrations of the species.

There are two major disadvantages limiting lasers described to achieve our goal:

- Pulse to pulse jitter
- Multimode regime of operation
1.4.2.1 Pulse to Pulse Jitter

It is well known that actively Q-switched lasers (i.e. instantaneous switching of quality factor) have good stability of pulse repetition rate at even high frequencies but in passively q-switched systems there is a presence of a strong jitter [23]. There are a number of techniques implemented to eliminate instability in pulse repetition rate. In case of a pulsed pumping the timing stability can be improved by applying as high peak power as possible for just long enough to produce an output pulse [16]. Pump pulses are turned on by an external clock and turned off when a Q-switched output pulse is detected minimizing thermal effects in passively Q-switched lasers because it minimizes efficiency losses due to spontaneous decay of the gain medium, leading to additional benefits in performance [16]. In a passively Q-switched laser using CW pumping just below threshold and then quickly raising it to its maximum value when an output pulse is desired leads to the greatest pulse-to-pulse timing stability [16]. Another approaches involve hybrid active/passive loss modulation [24] and external optical synchronization [25] resulting in timing jitter as low as 65 ps [26].

In this work we planned to eliminate pulse to pulse jitter in a passively q-switched laser by modulation of a pumping source with the frequency matching pulse repetition rate of passively Q-switched pulses.

1.4.2.2 Single-Frequency Regime of Operation:

Q-switched lasers operating in more than one longitudinal or transverse mode exhibit intensity modulated output pulses due to mode beating, however single frequency regime provides high quality smoothly varying temporal pulse profile [16]. High quality of the laser pulse profile in temporal and spectral domain is in a strong demand for a lot
of applications including high resolution ranging [27], altimetry [28], light detection, ranging (LIDAR) and sensing.

There are a number of methods to obtain single frequency regime of operation. To ensure single-transverse-mode of operation the pumping beam should coincide with the cavity mode of the laser. Single-frequency operation of a Q-Switched laser could be obtained usually by incorporating frequency selective optical elements in the laser resonator. Actively Q-switched laser pulse consists of a strongest cavity modes that start to build up from spontaneous emission as soon as Q-Switch losses are switched off, and it takes a number of round trips to extract the stored energy from the laser resonator. Spectral content of the output pulse depends on a gain and build-up time of each cavity mode [16].

In [16] authors suggest that to ensure a single-frequency operation of an actively Q-switched laser the number of photons in the primary mode must be at least 100 times greater than the number in any other mode by the time the output pulse forms. An early work [29] had shown that a factor of ten is enough to ensure single-frequency operation since the primary mode will extract most of the stored energy in the cavity, leaving very little energy for other modes.

An alternative criterion [30] for single-frequency operation of passively Q-Switched lasers considers that the build-up time difference between two competing modes must be comparable with or greater than the laser pulse duration. The strongest mode will extract most of the stored energy in the cavity suppressing the growth of the competing mode.
In this work we will adopt theoretical model [30] to our laser systems to analyze and optimize laser cavity to ensure a single frequency regime of operation.

**1.4.3.3 Thesis research goals and dissertation outline**

The major research goal of this effort was development of new spectroscopic lasers operating in the mid-IR spectral range for high sensitive organic molecule detection systems. There are two major approaches for generation of mid-IR laser radiation. First approach is based on non-linear frequency conversion of the available pump lasers. Second approach is based on direct mid-IR lasing. For this approach, the broadly tunable TM doped II-VI wide band semiconductor materials are excellent candidates for gain media. In spite of different physical principals, both approaches need pump lasers operating in the 1.5-2.1 μm spectral range. Depending on the type of detection platform, the pump source for tunable laser system should operate either in CW mode or Q-switched mode at high repetition rate ≥100 Hz. The CW pump source based on Er\(^{3+}\) (@1.6 μm) and Tm\(^{3+}\) (1.9 μm) fiber lasers with output power of hundreds of Watts are commercially available. These fiber lasers are well established for pumping Cr\(^{2+}\) tunable solid state mid-IR lasers. However, Q-switched solid state lasers operating at high repetition rate in the 1.5-2.1 μm spectral range require special development based on specific requirements of the detection systems. In addition, the nonlinear frequency conversion systems with CW pumping are very complicated and not reliable. Therefore, one of the specific goals of the research was development of fiber pumped actively Q-switched Er\(^{3+}\) and Ho\(^{3+}\) solid state lasers operating at high repetition rate which could be used as pump sources for tunable mid-IR laser systems and in the nonlinear frequency conversion devices. Resonantly pumped actively Q-switched solid state lasers
demonstrate high efficiency at high repetition rate. However, these laser systems have more complicated design than passively Q-switched lasers. In some spectroscopic applications where compactness of system design is crucial, the passively Q-switched lasers could demonstrate better performance. Especially, the single frequency oscillation in the passively Q-switched lasers could be demonstrated without any additional spectral selectors, while actively Q-switched solid state lasers require additional intra cavity elements to control single frequency oscillation. Among different passive Q-switchers for Er$^{3+}$ and Ho$^{3+}$ solid state lasers, the transition metals doped II-VI semiconductors are excellent candidates due to high absorption cross-sections in the 1.3-2.1 μm spectral range and absence of the excited state absorption. Therefore, second specific goal was to developed single frequency oscillation of the passively Q-switched Er$^{3+}$ and Ho$^{3+}$ lasers; and to understand the roles of the physical parameters of the passive Q-Switchers, gain elements; laser cavity; and thermal management for single frequency oscillation. These two specific goals of the research were addressed in the second chapter of the thesis. Third Chapter of the thesis describes development of the tunable single frequency solid state laser for spectroscopic applications. It includes: third specific goal to develop single frequency Cr:ZnSe laser capable to operate in broadband 2-3 μm spectral range with narrow linewidth of emission; and forth specific goal to study mechanisms of fine tuning of single frequency lasing around selected emission line to achieve wavelength modulation requirements for spectroscopic detection systems. Last chapter of the thesis includes conclusions and proposed future work.
CHAPTER II

Ho\textsuperscript{3+}:YAG AND Er\textsuperscript{3+}:YAG LASERS

2.1 Ho\textsuperscript{3+}:YAG Lasers

The objective of this work was to perform a comparative investigation of the performance of a fiber-bulk hybrid 2.09 \textmu m Ho:YAG laser in CW, active, and passive Q-switched regimes of operation with the use of our high quality Cr2+:ZnSe crystals [31] as saturable absorbers for passive Q-Switch measurements.

2.1.1 CW and Actively Q-Switched Regimes of Operation

An unpolarized 30 W Tm doped fiber laser (Model TLR-30-1908, IPG Photonics Corp.) with a collimated, diffraction-limited 1908 nm beam with diameter of 1.1 mm was used as a pumping source. The output spectrum of the Tm fiber laser measured with the Acton Research Spectrometer SpectraPro 300i is shown in Figure 6.

![Figure 6. The output spectrum of the Tm fiber laser.](image-url)
A Ho:YAG rod of 5mm in diameter and 40 mm in length with holmium concentration of 0.5 % was used as an active medium. Absorption and emission cross-sections of Ho:YAG are depicted in Figure 7. One can see from the Figure 7 that Tm laser radiation of 1908 nm corresponds to the strongest absorption line of Ho:YAG shown in Figure 7 (blue curve).

![Figure 7](image)

Figure 7. The absorption (blue) and emission (red) cross-sections of Ho:YAG.

Output characteristics of CW and acousto-optical (AO) Q-switched Ho:YAG lasers were studied with two types (short and long) of cavity configurations.

2.1.1.1 Highly-Efficient Ho:YAG Laser Configuration

A short cavity configuration is depicted in Figure 8. Here, the laser cavity was shortened to the minimum possible length (limited by the sizes of AO modulator and Ho:YAG crystal) and the pump beam was focused into the Ho:YAG crystal with a
200 mm focal length lens. The laser cavity was formed by a 100% back mirror with a radius of 0.5 m, a plane output coupler with 50% reflectivity at 2.1 µm, and a 45°-dichroic flat folded mirror (FM) with high transparency at 1.9 µm and a high reflection at 2.1 µm. A plane-parallel CaF₂ plate was used as an intracavity Brewster polarizer. A thermo-electrically cooled (TEC)/air-cooled AO modulator (based on SiO₂) was used as an active Q-switch.

Figure 8. Optical scheme of the highly-efficient Ho:YAG laser.

This configuration allowed obtaining maximum output power of about 10 W in CW mode at a pump power of approximately 22 W, leading to a real efficiency of about 50% (Figure 9a). Average output power versus incident pump power in acousto-optical Q-switched regime of operation at 10 kHz repetition rate is plotted in Figure 9b. The graphs contain four experimental data sets. The linear fits to the experimental data show the slope efficiencies of 50% for both CW and active Q-switched regimes of operation. Experiments indicate that further increase of the output mirror reflectivity does not lead to increase of the laser efficiency.
Figure 9. Average output power versus incident pump power in CW (top graph) and 10 kHz Q-switched (bottom graph) regimes of operation. The graphs contain four experimental data sets. The linear fits to the experimental data show the slope efficiencies of 50% for both CW and Q-switched regimes of operation.
2.1.1.2 High-Energy Ho:YAG Laser Configuration

Schematic diagram of an experimental setup with long cavity is depicted in Figure 10. Power characteristics for repetition rates from 100 Hz up to 10 kHz of Q-switched modulation were measured. In contrast to the previous design shown in Figure 8 of high-efficient Ho:YAG laser, where the optimum output mirror reflectivity was 50 %, this configuration allows to achieve high energy pulses at low repetition rates with the optimal output mirror reflectivity of 30 %.

The input-output power dependence of an actively Q-switched Ho laser is shown in Figure 11 (a) for a modulation frequency of 100 Hz and 30 % output coupler. As a comparison, Figure 11 (b) illustrates the output power vs. pump power dependence for the CW regime when the AO-modulator is turned off.
Figure 11. Output-input characteristics of an actively Q-switched Ho:YAG laser.
One can see from graphs in Figure 11 that there is a dip at pump power of 20 W which caused most likely by thermal lens in a Ho:YAG active medium rod. The dependence of the maximum output energy on the repetition rate of modulation is shown in Figure 12.

![Maximum output energy vs repetition rate](image)

**Figure 12.** Ho:YAG output energy vs. modulation frequency.

As seen in Figure 12, output energy increases with a decrease in the repetition rate. Maximum output energy of 15 mJ was achieved at a repetition rate of 100 Hz and a pump power of 22 W. Besides maximum power of Tm laser is 30 W the incident power was limited due to optical damage of dichroic folded mirror at high energy pulses.
2.1.2 **Passively Q-Switched Regime of Operation**

Two chromium doped ZnSe (Cr\(^{2+}:\text{ZnSe}\)) crystals with transparency of 70% and 94% have been used as saturable absorbers to investigate passive Q-switching of a laser resonator shown in Figure 13. The difference between this resonator and cavity shown in Figure 8 is that Cr\(^{2+}:\text{ZnSe}\) crystal was placed instead of CaF\(_2\) Brewster plate and AO modulator was removed. Passive Q-SW saturable absorbers were prepared by doping of ZnSe crystals from the gas phase in a sealed quartz tube at 1000\(^\circ\)C during two weeks. Figure 14 represents transmission spectra for 94% crystal sample.

![Figure 13. Optical scheme of the high-energy passively Q-switched Ho:YAG laser.](image)

Figure 13. Optical scheme of the high-energy passively Q-switched Ho:YAG laser.
Figure 14. Transmission spectrum of Cr:ZnSe crystal with 94 % transmission at 2.1 μm.

Output input power characteristics for the passively Q-switched Ho:YAG laser with 50 % reflectivity plane mirror as an output coupler and passive Q-Switched crystal with transmission of 94 % at a 2.1 μm holmium ions emission wavelength is shown in Figure 15.
Figure 15. Output power of a passively Q-Switched Ho laser with 94% transmission of saturable absorber.

Tm pumping laser allows delivering of 30 W, however, the incident power was limited to 20 W to prevent optical damage of the dichroic folded mirror. Figure 16 represents pulse repetition rate dependence versus pump power.
Figure 16. Repetition rate of a passively Q-Switched Ho laser with 94% transmission of saturable absorber.

The typical shape of a pulse profile of a passively Q-Switched Ho laser at a pump power of 19 W is shown in Figure 17.
Figure 17. Q-Switched Ho laser pulse profile.

It is evident from Figure 17 that the pulse duration of a passively Q-SW Ho laser is about 120 ns. Figure 18 demonstrates the temporal behavior of Ho laser pulses at pump power of 17 W. The time between pulses is about 0.2 ms (Figure 18). This corresponds to a repetition rate frequency of 5 kHz. A variation in amplitude of Ho Q-Switched pulses (Figure 18) was due to regime of multiple transverse modes of operation.
Second Cr\textsuperscript{2+}:ZnSe crystal with initial transmission of 70 % at 2.1 μm was used to obtain passive Q-switching of a Ho:YAG laser in a short cavity depicted in Figure 13. Here incident power was limited to prevent optical damage of a folded mirror and Q-Switch crystal. Figure 19 represents dependence of an average output power versus pump power.

Figure 18. Temporal profile of passively Q-Switched Ho laser output power.
Figure 19. Average output power versus incident pump power in Q-switched regime of operation for 70% transmission of a saturable absorber.

Figure 20 and Figure 21 represent pulse repetition rate and pulse energy versus pump power, respectively.

Figure 20. Pulse repetition rate versus incident pump power in Q-switched regime of operation for 70% transmission of a saturable absorber.
Figure 21. Pulse energy versus incident pump power in Q-switched regime of operation for 70% transmission of a saturable absorber.

Maximum pulse energy obtained was about 3 mJ at 20 W pumping power (see Figure 21). At pump power above 20 W output lasing was unstable due to a most likely mode mismatch caused by a thermal lens in the active medium and saturable absorber. Input power was limited to prevent optical damage of a folded mirror and Q-Switch crystal during unstable operation. Pulse profile for input power of 20 W corresponding to pulse energy of 2.94 mJ is shown in Figure 22.
One can see from Figure 22 that the pulse duration is about 7 ns at FWHM. It must be noticed that pulse duration was the same over the whole range of incident pumping powers. A fiber-bulk Ho:YAG passively Q-Switched single frequency laser setup designed in this section shows good stability of output parameters over a 4 hour time period.
Among nonlinear crystals Zinc Germanium di-Phosphate (ZGP) has outstanding fundamental properties as a mid-IR nonlinear crystal. It is especially suitable for high average power applications throughout the infrared region. The large nonlinear coefficient of ZGP, which is approximately 8.8 times that of periodically poled lithium niobate (PPLN), makes it one of the most efficient nonlinear crystals known. Because of some residual absorption below 1.8 µm wavelength, ZGP pump wavelength should be chosen at 2 µm or higher. Thus, 2 µm holmium lasers are good candidates for this purpose. An experimental setup depicted in Figure 23 was realized to investigate frequency conversion in ZGP Optical Parametric Oscillator (OPO). Unfocused radiation of the passively Q-switched Ho:YAG laser (with pulse energy of 2 mJ and repetition rate of 1 kHz ) was directed into the OPO cavity by a 45° dichroic mirror (HR at 2.1 µm) through a Silicon wafer placed at Brewster angle for 2.1 µm. Pump beam spot diameter at crystal surface was equal to 1mm. The OPO cavity consisted of one golden plane end-mirror and one plane dielectric input-mirror with transmission of ~50 %. ZGP OPO crystal of 20 mm in length having cut for type I OOE interaction (θ=49.5°, φ=0) was placed in the 4cm long resonator cavity. The crystal has antireflection coatings on both faces for high transmission over 2.8 - 6 µm spectral range. This crystal is mounted on a rotational stage providing rotation in the vertical plane for realization of the phase matching conditions at various output wavelengths.
Figure 23 Experimental setup for nonlinear conversion of Ho:YAG laser emission by ZGP OPO.

Signal and Idler generated in the OPO were directed to spectrograph by a Silicon wafer through a filter. An infrared filter has been used to cut off pumping wavelengths. Additional dichroic mirror was used for separation of the residual Tm-fiber laser and Ho:YAG laser radiations. An experimental data of the tunable mid IR laser obtained using optical scheme depicted in Figure 23 are shown in Figure 24 by blue (signal) and red (Idler) dots. The OPO phase matching condition calculated with the use of Select Non-Linear Optics (SNLO) ver. 4.6 software under Ho:YAG pumping (2.09 µm) is shown in the Figure 24a by blue (signal) and red (idler) curves. Figure 24b demonstrates spectra of the tunable mid-IR oscillation in the 2.6 - 8.6 µm spectral range measured with a low resolution spectrometer.
Figure 24 (A) Phase matching condition for the ZGP crystal under 2.09 μm pumping wavelength (curve), and experiments measurements of the signal (blue dots) and idler (red dots) wavelengths for different phase matching angle. (B) Output spectra of the tunable ZGP-OPO measured with a low resolution spectrometer.
One can see from the Figure 24 that holmium laser emission was down-converted by ZGP OPO Type I interaction into a broad spectrum of radiation from 2.6 up to 8.6 µm. The results show a satisfactory agreement between experiment and theoretically calculated data.

In our preliminary experiments the incident pump-energy was below 2 mJ. The quantum conversion efficiency from pump radiation to 3.8 µm signal radiation was 11%.

2.1.4 Thermal Management

2.1.4.1 Introduction

Presence of a thermal lensing in crystals and glasses limits their flexibility to serve efficiently at different pumping power and temperature. The laser resonator would be efficiently operating only at particular level of optimized pumping power for a fixed configuration. Temperature gradient in active media creates gradient of refractive index which forms a “thermal lens”. Realization of good heat dissipation can minimize thermal lensing effect. Analysis of a thermal contact resistance across a copper heat sink - ZnSe interface has been performed. In this part of the work we are analyzing conditions of optimal heat dissipation minimizing parasitic thermal effects in passive Q-Switch crystals and active media based on Cr:ZnSe materials.

2.1.4.2 Experimental Procedure

Thermal resistance is an important parameter for thermal management. In our experiments we measured thermal conductivity of different samples consisted from copper blocks and semiconductor crystals. From the comparison of thermal conductivity
of samples with different geometry we were able to calculate thermal contact resistivity
between semiconductor crystals and copper blocks. Four different types of interface
structures have been investigated. They consisted of indium foil, thermal grease (Part
#120-2 WAKEFIELD), Cu thin film deposited on ZnSe, and Ag thin film deposited on
ZnSe by electrolyze. All 0.5 inch ZnSe cylindrical samples were soldered or pressed
between 0.5 inch Cu disks. A summary of the sample preparation details is presented
below in Table 3.

Table 3 Summary of samples used in measurements of thermal contact resistance across a
copper heat sink - ZnSe interface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnSe thickness</th>
<th>Contact interface between flat sample surfaces and Copper disks</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>No ZnSe</td>
<td>Two copper disks were fixed together without ZnSe crystal</td>
</tr>
<tr>
<td>#2</td>
<td>3.3 mm</td>
<td>ZnSe crystal was fixed between copper disks with Indium-film</td>
</tr>
<tr>
<td></td>
<td></td>
<td>interface</td>
</tr>
<tr>
<td>#3</td>
<td>7.3 mm</td>
<td>ZnSe crystal was fixed between copper disks with Indium-film</td>
</tr>
<tr>
<td></td>
<td></td>
<td>interface</td>
</tr>
<tr>
<td>#4</td>
<td>3.3 mm</td>
<td>Copper film was deposited on flat ZnSe surfaces and then the</td>
</tr>
<tr>
<td></td>
<td></td>
<td>crystal was soldered to the copper disks</td>
</tr>
<tr>
<td>#5</td>
<td>3.3 mm</td>
<td>Silver thin film was deposited by electrolyze and then the crystal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>was soldered to the copper disks</td>
</tr>
<tr>
<td>#6</td>
<td>3.3 mm</td>
<td>ZnSe crystal was fixed between copper disks with thermal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>grease</td>
</tr>
</tbody>
</table>

The thermal conductivity of the samples was measured using H-6862 (Hampden)
thermal conductor experimental setup. Some of the soldered samples and samples with
copper film deposited on the ZnSe crystals are shown in Figure 25. The experimental
details are shown in Figure 26. Heat flow through the samples was controlled by 6
thermocouples (TC) (3 TC on heater and 3 TC cold sides). The temperature drop in the sample was calculated as the difference between TC4 and TC3. Sample #1 (without ZnSe crystal) was used as a reference value to exclude geometrical factor influence.

Figure 25. Some soldered samples and samples with copper film on ZnSe crystals.

Figure 26. Experimental details of arrangement for measurement of thermal conductivity.

2.1.4.3 Experimental Results

The results obtained are summarized in Table 4 below. As it is apparent, the optimal radius of the ZnSe rod for the studied interfaces is in the 2-3 mm range. Smaller rod radius will result in decreasing of the interface area and increasing of the temperature increment at the crystal surfaces.
Table 4. Summary of the results on thermal contact resistance measurements and optimal rod radius.

<table>
<thead>
<tr>
<th></th>
<th>Sample</th>
<th>Power passed through sample</th>
<th>$\Delta T$ (T3-T4)</th>
<th>$\Delta T$, normalized on the heat power</th>
<th>$\Delta T_{cal}$-$\Delta T_{#1}$</th>
<th>Thermal contact conductance, W/m²K</th>
<th>Optimal Rod Radius $R_{cr} = K/\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>No ZnSe, Cu-0.5 disks</td>
<td>1 a.u.</td>
<td>40 F</td>
<td>40 F</td>
<td>0 F</td>
<td></td>
<td>3mm</td>
</tr>
<tr>
<td>#2</td>
<td>ZnSe, 3.3 mm +In Foil</td>
<td>0.66 a.u.</td>
<td>68.7 F</td>
<td>104.1 F</td>
<td>64.1F</td>
<td>$5.7 \times 10^3$</td>
<td>3mm</td>
</tr>
<tr>
<td>#3</td>
<td>ZnSe, 7.3 mm +In Foil</td>
<td>0.56 a.u.</td>
<td>74.8 F</td>
<td>130.8 F</td>
<td>90.8 F</td>
<td>$5.7 \times 10^3$</td>
<td>3mm</td>
</tr>
<tr>
<td>#4</td>
<td>ZnSe, 3.3 mm +Ag electrolyze +soldered</td>
<td>0.71 a.u.</td>
<td>63.2 F</td>
<td>89 F</td>
<td>49 F</td>
<td>$9.1 \times 10^3$</td>
<td>2 mm</td>
</tr>
<tr>
<td>#5</td>
<td>ZnSe, 3.3 mm +Cu deposited+soldered</td>
<td>0.70 a.u.</td>
<td>64.3 F</td>
<td>90.5 F</td>
<td>50.5 F</td>
<td>$8.6 \times 10^3$</td>
<td>2.1 mm</td>
</tr>
<tr>
<td>#6</td>
<td>ZnSe, 3.3 mm +thermal grease</td>
<td>0.70 a.u.</td>
<td>64.4 F</td>
<td>92.3 F</td>
<td>52.3F</td>
<td>$8 \times 10^3$</td>
<td>2.3 mm</td>
</tr>
</tbody>
</table>
A) Indium-foil contact

Temperature gradient for 3.3 and 7.3 mm crystal thickness was compared to estimate thermal contact conductance:

\[
\Delta T_{#2} = \Delta T_{\text{In, surfaces}} + \Delta T_{\text{ZnS 3.3 mm}} \\
\Delta T_{#3} = \Delta T_{\text{In, surfaces}} + \Delta T_{\text{ZnS 7.3 mm}}
\]

After subtraction one can estimate the temperature drop inside ZnSe crystal as:

\[
\Delta T_{#3} - \Delta T_{#2} = \Delta T_{\text{ZnS 7.3 mm}} - \Delta T_{\text{ZnS 3.3 mm}} = \Delta T_{\text{ZnS 3.3 mm}} \left(\frac{7.3}{3.3} - 1\right) = 26.7 F
\]

and

\[
\Delta T_{\text{ZnS 3.3 mm}} = \frac{26.7 F}{1.21} = 22.1 F
\]

Using this value the temperature drop in the two interfaces can be calculated as

\[
\Delta T_{#2} = \Delta T_{\text{In, surfaces}} + \Delta T_{\text{ZnS 3.3 mm}} = \Delta T_{\text{In, surfaces}} + 22.1 F = 64.1 F \\
\Delta T_{\text{In, surfaces}} = 42 F
\]

The thermal contact conductance can be calculated using the ratio:

\[
\frac{\Delta T_{\text{In, surface}} / 2}{\Delta T_{\text{ZnS 3.3 mm}}} = \frac{k/L}{2\chi} = \frac{42 F}{2 \cdot 22.1 F} = 0.95
\]
The thermal contact conductance of the other interfaces can be estimated similarly using the calculated value for temperature drop inside 3.3 mm ZnSe crystal.

**B) Thermal grease**

\[ \Delta T_{#6} = \Delta T_{GR} + \Delta T_{ZnS\,3.3\,mm} = 52.3F \]

\[ \Delta T_{GR\,surfaces} = 52.3F - \Delta T_{ZnS\,3.3\,mm} = 52.3F - 22.1F = 30.2F \]

\[ \frac{\chi_{Ag}}{\chi_{In}} = \frac{\Delta T_{in}}{\Delta T_{GR}} = \frac{42F}{30.2F} = 1.4 \]

**C) Ag electrolysis**

\[ \Delta T_{#4} = \Delta T_{Ag} + \Delta T_{ZnS\,3.3\,mm} = 49F \]

\[ \Delta T_{Ag\,surfaces} = 49F - \Delta T_{ZnS\,3.3\,mm} = 49F - 22.1F = 26.9F \]

\[ \frac{\chi_{Ag}}{\chi_{In}} = \frac{\Delta T_{in}}{\Delta T_{Ag}} = \frac{42F}{26.9F} = 1.6 \]

**D) Cu deposited+soldered**

\[ \Delta T_{#5} = \Delta T_{Cu} + \Delta T_{ZnS\,3.3\,mm} = 50.5F \]

\[ \Delta T_{Cu} = 50.5F - \Delta T_{ZnS\,3.3\,mm} = 50.5F - 22.1F = 28.4F \]

\[ \frac{\chi_{Cu}}{\chi_{In}} = \frac{\Delta T_{in}}{\Delta T_{Cu}} = \frac{42F}{28.4F} = 1.5 \]
As one can see from these calculations under the same condition the temperature drops on the different interfaces are as follows:

$$\Delta T_{in}: \Delta T_{Gr}: \Delta T_{Ag}: \Delta T_{cu} = 1: \frac{1}{1.4}: \frac{1}{1.6}: \frac{1}{1.5}$$

Or

$$\Delta T_{in} > \Delta T_{Gr} > \Delta T_{cu} > \Delta T_{Ag}.$$  

2.1.4.4 Conclusions

In this part of the research it was found that silver thin film deposited on ZnSe crystal by electrolysis provided the best thermal contact among studied interfaces. The thermal grease exhibits similar properties as silver and copper interfaces but much better than indium foil. Thermal grease was chosen as an interlayer thermal contact with heat sink for heat dissipation.
2.2 Er\textsuperscript{3+}:YAG Lasers

Er:YAG lasers operating at 1.6 μm eyesafe spectral range (\(^{4}I_{13/2} \rightarrow {^{4}I_{15/2}}\) transition) are widely used in a variety of medical, scientific, and military applications. Direct resonant pumping into \(^{4}I_{13/2}\) manifold by commercially available 1.532 μm Er-fiber lasers results in a small quantum defect of ~7 % and more than 80 %, efficiency of lasing [32].

2.2.1 CW vs. Passive Q-Switched Regime of Operation

Chromium doped zinc selenide crystals were successfully utilized as passive saturable absorbers due to their long relaxation lifetime of ~8 μs, peak absorption at 1.77 μm, absence of excited state absorption, and high cross-section of saturation ~ 10\(^{-18}\) cm\(^2\) [33]. Low cost assembly allows transforming few watts of CW power into repetitive pulses at sub megawatt peak power with few kilohertz repetition rate. The purpose of this study is to show capabilities of the Er:YAG laser to operate in passively Q-Switched mode of operation using Cr:ZnSe saturable absorber and compare it to CW regime.

2.2.1.1 Experimental Setup

Laser cavity configuration used in this experiment is depicted in Figure 27. The 5 mm pump beam from the ELM-15-1532 fiber laser (IPG Photonics Corp.) is focused into the Er:YAG laser rod (0.25 % at Er:YAG, 5mm×50mm) through dichroic flat 45-degree folding mirror (HR@1600-1700 nm, AR@1532 nm) by a 500 mm AR-coated focusing lens. The laser scheme is based on a semi-concentric cavity design with the 250 mm end mirror and 80 % output coupler (OC). Two chromium doped ZnSe crystals with initial transmission of 92.5 % and 95 % at 1645 nm served as saturable absorbers and were placed at Brewster angle 30 mm away from the dichroic mirror.
2.2.1.2 Results and discussion

Output-input power characteristics are depicted in Figure 28. One can see from the Figure 28 that the output power measured with the use of 95% transmission of passive Q-Switch crystal slightly exceeds one for 92.5% of transmission and is about 40% efficient with respect to pure CW (no Q-Switch crystals in the laser cavity) mode of operation. More efficient long cavity configuration was able to provide higher power of 7 W in CW mode. However, stable passively Q-Switched regime was not realized in long cavity for both Q-Switch crystals due to thermal effects causing optical damage of the cavity elements.
Figure 28. Input-Output power characteristics of Er:YAG laser.

Pulse repetition rate for passive regime of operation is depicted in Figure 29. It is clear from Figure 29 that pulse repetition rate for more transparent saturable absorber is higher. It must be noticed that there was a presence of the timing jitter which was about 10% of the repetition frequency. Output energy of passively Q-Switched pulses is depicted in Figure 30. It is obvious that denser saturable absorber provides higher output energy of the Q-Switched pulses.
Figure 29. Pulse repetition rate of Passively Q-Switched Er:YAG laser.

Figure 30. Output energy of the passively Q-Switched pulses.
Durations of the passively Q-Switched pulses are depicted in the Figure 31 for the whole range of pumping power. One can see from Figure 31 that pulse duration for a more transparent saturable absorber would be larger.

![Pulse duration graph](image)

Figure 31. Durations of the passively Q-Switched pulses.

### 2.2.2 Theoretical Modeling of Single Frequency of Operation

#### 2.2.2.1 Demand on Single Frequency Laser.

Q-switched Er:YAG lasers operating at 1.6μm “eye-safe” spectral range (4^I\textsubscript{13/2} → 4^I\textsubscript{15/2} transition) are widely used in a variety of sensing, medical, scientific, and range-finding applications. Direct resonant pumping into 4^I\textsubscript{13/2} manifold by commercially available 1.532 μm Er-fiber lasers results in a small quantum defect of ~7 % and more
than 80 %, efficiency of lasing. Chromium doped zinc selenide crystals can be utilized as effective passive saturable absorbers for Q-Switching of Er:YAG cavities. However, single frequency regime of operation of passively Q-Switched Er:YAG, essential for multiple practical applications, was difficult to realize without additional mode-selection elements in the cavity.

The simplicity and compactness of Cr:ZnSe passive Q-Switches is ideal for many industrial, military applications as well as for scientific research. An accuracy and quality of the measurements depend on laser pulse quality Gaussian-shape pulse profile without mode-beating induced amplitude fluctuations are essential for precise measurements and can be realized in a single frequency regime of laser operation. However, single frequency regime of operation with a small jitter was difficult to realize without additional mode-selection elements in the cavity.

2.2.2.2 Historical Background.

It was observed earlier [34] that utilization of saturable absorbers results in narrowing of the output spectra of the laser radiation. A single mode of operation is possible to achieve with combination of additional intracavity selective elements [29]. A theoretical idea explaining above phenomena was evaluated in [29]. Author focused attention on a parameter so-called mode “build up time” playing role in mode selection mechanism of passively Q-Switched lasers. A mode build-up time is a time necessary for the mode to achieve intensity from the noise to the value when saturable absorber starts to bleach. In a fast Q-Switched lasers adjacent modes starts to oscillate in about few tens of round trips just after a Q-Switch is opened. However in a slow (passively Q-switched) opening lasers it takes few hundreds of round trips for the modes to build up until
saturable absorber is bleached and the strongest mode will suppress the weakest ones [29]. Author suggests [29] a factor of ten in differences of adjacent modes intensities is enough to ensure single frequency of operation.

2.2.2.3. **Criterion for Single Frequency of Operation.**

In a recent paper [30] a theoretical and experimental study was performed to investigate conditions of single frequency of operation of Nd:YAG laser, using a saturable absorber based on F\(_2^−\) color centers in LiF crystal. A more corrected criterion for single mode of operation was introduced and it states that “difference in build-up time between any two longitudinal modes must be comparable with or greater than the pulse duration”.

2.2.2.4 **Criterion Limitation (constant inversion and non-periodic excitation).**

A direct resonant pulsed pumping was implemented in [35]. It must be noticed that in this [35] experimental setup every pumping pulse doesn’t contribute to kinetics process of the previous laser oscillation. With an assumption of constant population inversion an intracavity photon density of the rate equation could be simplified and solved for the build-up time differences between adjacent modes.

2.2.2.5 **Approach and Goal of Current Work.**

The purpose of this work was to verify whether theoretical modeling [30] proven for Nd:YAG laser passively Q-switched with LiF:F\(_2^−\) color center crystal is appropriate for Er:YAG laser passively Q-switched with Cr:ZnSe crystal. The goal is to realize conditions when a single mode of operation of passively Q-Switched Er:YAG laser will
be achieved without additional intra-cavity selective elements in the laser resonator. The result of this study is to formulate criterion for single frequency of operation of passively Q-Switched Er:YAG laser for CW excitation.

2.2.2.6 Dynamic Picture of the Laser Oscillation Under CW Pumping.

Dynamic picture of the processes playing role in laser oscillations is depicted in Figure 32. Intracavity intensity $I$ starts to rise from the noise $I_0$ to value of saturation intensity of saturable absorber $I_s$ as soon as threshold $N_{th}$ conditions achieved (when cavity gain approaches value of resonator losses). At this point a saturation of passive Q-Switch occurred (so-called bleaching of the saturable absorber) resulting in no absorption losses contribution during lifetime of the absorber ($\tau_{abs} \sim 6 \mu$s for Cr:ZnSe crystal). Absence of the losses in a passive Q-Switch saturable absorber comes from the fact that there are almost no active centers in the ground state. Negligible amount of the ions in the ground state of the absorber will be maintained during lifetime of the upper excited level making it transparent to the intracavity modes. An energy stored in the laser resonator will be released as a giant pulse dropping inversion in the active medium from its maximum value $N_{max}$ to the minimum value $N_{min}$. This process will continue periodically with pulse repetition rate $f$. It is obvious that oscillation in this regime could not be faster than $1/\tau_{abs}$. 
Figure 32. Dynamic picture of the laser oscillation.

Where:

$N_{th}$ - Threshold population inversion

$f$ – Pulse repetition rate

$I_s$ – saturation intensity of the saturable absorber

$\tau$ - Q-Switched pulse duration

$n_{abs}$ – population inversion in saturable absorber
\( \tau_{\text{m}} \) - mode rise time (when intracavity mode intensity rise from noise \( I_0 \) to saturation level \( I_s \) after threshold condition)

\( I_0 \) - Average Intra cavity oscillation seeding intensity at the beginning of the new pulse oscillation

\( I_s \) - Average Intra cavity oscillation intensity at the beginning of passive q-switch saturation

2.2.2.7 Oscillation build-up time (Solution for pulsed excitation)

In the experiment conducted by [35] a pumping pulse accumulates absorbed energy in the upper laser lever. With assumption of constant passive Q-Switch losses until absorber bleaching and neglecting spontaneous emission, the rate equation for intracavity intensity of “n” mode of laser resonator as in [36] can be described as follows:

\[
\frac{dI_n(t)}{dt} = \frac{I_n(t)}{t_{rt}} \left[ 2\sigma_n l_g N(t) - L_n \right],
\]

(1)

Where:

\( I_n \) - is intracavity intensity of the \( n \)th longitudinal mode,

\( \sigma_n \) - is emission cross-section of the laser mode \( n \);

\( l_g \) - is gain element length;

\( N(t) \) - is population inversion in the gain element;

\( L_n \) - is the round-trip loss (includes output coupler transmission, unsaturated absorber transmission \( T_0 \), and all other contributed losses);

\( t_{rt} \) - is the round-trip transit time.
The $Q$-switched pulse starts to build up as soon as the threshold conditions are satisfied and continues until time $t_{sn}$, when the saturable absorber starts to bleach. With assumption of constant initial population inversion $N_i$ during this period of time and being slightly greater than the threshold inversion $N_{th}$, the rate equation (1) could be integrated, and becomes as follows:

$$I(t_{sn}) = I_0 \exp \left( \left[ 2\sigma_n l_g N_i - L_n \right] \frac{t_{sn}}{tr} \right), \quad (2)$$

Where:

$I_0$ is the initial intracavity intensity, which is assumed to be the same for all modes, and

$$N_i = N_{th} (1 + \varepsilon) \quad \text{for} \quad \varepsilon \ll 1, \quad (3)$$

The population inversion, $N_{th}$, can be determined from the threshold condition:

$$\exp \left( \left[ 2\sigma_n l_g N_{th} - L_n \right] \right) = 1, \quad (4)$$

Author of the paper [30] suggested that saturation intensities (energies) for two nearest mode are equal:

$$I_{sn}(t_{sn}) = I_{sm}(t_{sm}), \quad (5)$$

It is a reasonable assumption since

$$\Delta \nu_{nm} = \frac{1}{2L_{cav}} = 0.05 \text{ cm}^{-1} \approx 0.011 \text{nm},$$

And absorption bandwidth of the passive Q-Switch is ~1000 nm. Then equations (2) and (5) can be combined as follows:

$$\left[ 2\sigma_n l_g N_i - L_n \right] t_{sn} = \left[ 2\sigma_m l_g N_i - L_m \right] t_{sm}, \quad (6)$$
Build-up time of the $n$’th mode from equation (6) will be:

$$t_{sn} = t_{sm} \frac{2\sigma_m l_g N_{i-L_m}}{2\sigma_n l_g N_{i-L_n}} \quad (7)$$

Then the buildup time difference between adjacent modes looks like:

$$\Delta t_s = t_{sn} - t_{sm} = t_{sm} \frac{2\sigma_m l_g N_{i-L_m}}{2\sigma_n l_g N_{i-L_n}} - t_{sm} = t_{sm} \frac{2(\sigma_m - \sigma_n) l_g N_{i-(L_m-L_n)}}{2\sigma_n l_g N_{i-L_n}} \quad (8)$$

Taking into account $L_m = L_n$, equation (8) is simplified to:

$$\Delta t_s = t_{sm} \frac{2(\sigma_m - \sigma_n) l_g N_{i}}{2\sigma_n l_g N_{i-L_n}} = t_{sm} \left( \frac{\sigma_m - \sigma_n}{\sigma_n} \right) \left[ \frac{2 l_g \sigma_n N_{i}}{2\sigma_n l_g N_{i-L_n}} \right] = t_{sm} \left( \frac{\sigma_m - \sigma_n}{\sigma_n} \right) \left[ 1 + \frac{1}{\varepsilon} \right] \quad (9)$$

From the equation (2) $t_{sn}$ can be calculated as:

$$t_{sn} = t_{rt} \ln \left( \frac{I(t_{sn})}{I_0} \right) \frac{1}{2\sigma_n l_g N_{th} \varepsilon} \quad (10)$$

Finally, from (9) and (10) the buildup time difference could be expressed as:

$$\Delta t_s = t_{rt} \ln \left( \frac{I_s}{I_0} \right) \frac{1}{2\sigma_n l_g N_{th}} \left( \frac{\sigma_m - \sigma_n}{\sigma_n} \right) \left[ 1 + \frac{1}{\varepsilon} \right] \quad (11)$$

Hypothesis of single frequency regime of oscillation from [30] states: “The buildup time difference between any two longitudinal modes of the laser resonator should be comparable with or greater than the laser pulse duration to ensure single-frequency operation”. This criterion was experimentally proved [30] for pulsed diode pumped Nd:YAG laser, passively Q-Switched using a saturable absorber based on $F_2^-$ color centers in LiF crystal.
2.2.2.8 Oscillation Build-up Time Modeling for CW Pumping (Current work).

CW pumping provides constant feeding of the upper laser level. So the above equations describing kinetic processes should be modified to match CW pumping conditions. One can see from the dynamic picture that laser pulse starts to build-up as soon as threshold population inversion \(N_{th}\) is reached and continues until saturable absorber starts to bleach. Assuming negligible contribution of spontaneous emission to the inversion population rate and linear approximation of the inversion on the short time scale just after threshold the dependence of the population inversion could be represented as:

\[
N(t) = N_{th(n)} + \frac{dN}{dt} * t \quad (12)
\]

Kinetics of the population inversion and laser oscillation is depicted in Figure 33.

It is obvious from Figure 33 that contribution to the population inversion during rise time would be:

\[
\Delta N = \left(\frac{dN}{dt}\right) \tau_{sn}, \quad (13)
\]

Also it is clear that rise time difference between adjacent modes is:

\[
\Delta t_s = t_{sn} - t_{sm} = (\delta \tau_{th} + \tau_{sm}) - \tau_{sn}, \quad (14)
\]

Where \(\tau_{sn}\) and \(\tau_{sm}\) - mode rise time (when intracavity mode intensity rises from noise \(I_0\) to saturation level \(I_s\), after threshold condition); and \(\delta \tau_{th}\) - time delay between moments \(t_{th(n)}\) and \(t_{th(m)}\) when modes “m” and “n” reach their threshold levels \(N_{th(n)}\) and \(N_{th(m)}\), respectively.
Figure 33. Dynamic picture of the population inversion (top) and laser oscillation (bottom). $N_{\text{max}}$ is a population inversion at an onset of saturable absorber bleaching; $N_{\text{min}}$ - residue of the inversion after Q-Switch pulse extraction; $\delta \tau_{\text{th}}$ – time delay for adjacent longitudinal modes to achieve a threshold value of inversion. $N_{\text{th}}^{\text{cav}}$ is a cavity threshold with saturated passive Q-Switch. Dash-dotted line represents dynamics of the threshold inversion in the cavity.

Threshold condition for oscillation to start to build up is:

$$2\sigma_n l_g N_{\text{th}(n)} = L_n \quad (15)$$

Considering contribution of losses only from output coupler and double pass absorption in the passive Q-Switch the relation above will be:

$$2\sigma_n l_g N_{\text{th}(n)} = L_n = -\ln(R_{oc} T_0^2). \quad (16)$$
Where $R_{oc}$ – is reflection of output coupler. Taking into account $L_m = L_n = L$, the difference between population inversion of adjacent modes will be:

$$\delta N_{th} = N_{th(m)} - N_{th(n)} = \frac{L}{2l_g} \frac{(\sigma_m - \sigma_n)}{\sigma_m \sigma_n} \approx \frac{L}{2l_g} \frac{(\sigma_m - \sigma_n)}{\sigma_n^2}.$$  \hspace{1cm} (17)

Then

$$\delta \tau_{th} = \frac{\delta N_{th}}{(dN/dt)} \approx \frac{L}{2l_g} \frac{(\sigma_m - \sigma_n)}{\sigma_n^2} \frac{1}{(dN/dt)}.$$  \hspace{1cm} (18)

After threshold condition achieved the intracavity intensity of “n” and “m” mode could be rewritten as:

$$\frac{dl_n(t)}{dt} = \frac{l_n(t)}{\tau_{rt}} [2\sigma_n l_g \left(N_{th(n)} + \frac{dN}{dt} t \right) - L_n] = \frac{l_n(t)}{\tau_{rt}} [2\sigma_n l_g \left(\frac{dN}{dt} t \right)].$$  \hspace{1cm} (19)

Expression (19) has a solution:

$$\ln \left(\frac{l_n(t)}{l_0}\right) = \left[2\sigma_n l_g \left(\frac{dN}{dt}\right) \right] \frac{t^2}{2\tau_{rt}},$$  \hspace{1cm} (20)

Or

$$l_n(t) = l_0 \exp \left(2\sigma_n l_g \left(\frac{dN}{dt}\right) \frac{t^2}{2\tau_{rt}}\right) = l_0 \exp \left(2\sigma_n l_g \Delta N \frac{t^2}{2\tau_{rt}\tau_{sn}}\right).$$  \hspace{1cm} (21)

Oscillation rise time of “n” mode could be estimated from the following equation:

$$l_s(t_{sn}) = l_0 \exp \left(2\sigma_n l_g \left(\frac{dN}{dt}\right) \frac{t_{sn}^2}{2\tau_{rt}}\right) = l_0 \exp \left(2\sigma_n l_g \Delta N \frac{t_{sn}^2}{2\tau_{rt}}\right).$$  \hspace{1cm} (22)

So that:

$$t_{sn} = \tau_{rt} \ln \left(\frac{l_s}{l_0}\right) \frac{2}{2\sigma_n l_g \Delta N} = \tau_{rt} \ln \left(\frac{l_s}{l_0}\right) \frac{1}{2\sigma_n l_g N_{th} \left(\frac{2N_{th}}{\Delta N}\right)},$$  \hspace{1cm} (23)

Taking into account that $l_s$ and $l_0$ for both modes are the same we can write:

$$\sigma_n t_{sn}^2 = \sigma_m t_{sm}^2$$  \hspace{1cm} (24)
Then
\[ \tau_{sm}^2 - \tau_{sn}^2 = (\tau_{sm} - \tau_{sn})(\tau_{sm} + \tau_{sn}) \approx (\tau_{sm} - \tau_{sn})2\tau_{sn}, \quad (25) \]

And also
\[ \tau_{sm}^2 - \tau_{sn}^2 = \tau_{sn}^2 \left( \frac{t_{sm}^2}{t_{sn}^2} - 1 \right) = \tau_{sn}^2 \left( \frac{\sigma_n - \sigma_m}{\sigma_m} - 1 \right) = \tau_{sn}^2 \frac{(\sigma_n - \sigma_m)}{\sigma_m}. \quad (26) \]

So that:
\[ (\tau_{sm} - \tau_{sn}) = \frac{\tau_{sn}}{2} \frac{(\sigma_n - \sigma_m)}{\sigma_m} = \frac{\tau_{sn}}{2} \frac{(\sigma_n - \sigma_m)}{\sigma_m} \approx \frac{\tau_{sn}}{2} \frac{(\sigma_n - \sigma_m)}{\sigma_n}, \quad (27) \]

Finally
\[ \Delta t_s = \delta \tau_{th} + (\tau_{sm} - \tau_{sn}) = \frac{L}{2l_g} \frac{(\sigma_m - \sigma_n)}{\sigma_n^2} \frac{1}{(dN/dt)} + \frac{\tau_{sn}}{2} \frac{(\sigma_n - \sigma_m)}{\sigma_n} = \]
\[ \approx \tau_{sn} \frac{(\sigma_n - \sigma_m)}{\sigma_n} \left[ \frac{N_{th(n)}}{(dN/dt)\tau_{sn}} \right] = \tau_{sn} \frac{(\sigma_n - \sigma_m)}{\sigma_n} \left[ \frac{N_{th(n)}}{\Delta N} \right] = \Delta t_s, \quad (28) \]

Simplifying the last equation results in:
\[ \Delta t_s = \frac{(\sigma_n - \sigma_m)}{\sigma_n} \left[ \frac{N_{th(n)}}{(dN/dt)} \right]. \quad (29) \]

For adjacent modes \( \delta \nu = \frac{1}{2l_{cav}} \ll \Delta \nu \) so the modal gain difference:
\[ \frac{(\sigma_n - \sigma_m)}{\sigma_n} = \left( \frac{1}{\Delta \nu L} \right)^2, \quad (30) \]

The only unknown in equation (29) is the ratio \( \frac{N_{th(n)}}{(dN/dt)} \). There are several ways to estimate this value. The lowest limit could be estimated from the extended linear
approximation when population inversion growth is approximated to be a linear function not only on small interval ~ $t_{sn}$, but the whole period from $N_{min}$ to $N_{max}$ (see Figure 32.). According to this assumption a population inversion rate will be:

$$\frac{dN}{dt} = \frac{(N_{max} - N_{min})}{T_{period}} = (N_{max} - N_{min}) f$$  \hspace{1cm} (31)$$

To calculate this value one need $N_{max}$ and $N_{min}$. Equation (16) gives:

$$N_{max} \approx N_{th(n)} = -\frac{ln(R_{out} T_0^2)}{2\sigma n l_g}$$  \hspace{1cm} (32)$$

After saturation of the passive Q-Switch ($T_0=1$) the cavity population inversion threshold will be:

$$N^{Qs}_{th} = -\frac{ln(R_{out})}{2\sigma n l_a}$$  \hspace{1cm} (33)$$

Then the initial inversion ratio for QS pulse could be estimated as:

$$r = \frac{N_{max}^{Qs}}{N^{Qs}_{th}} = -\frac{ln(R_{out} T_0^2)}{ln(R_{out})} = 1 + \frac{ln(\tau_0^2)}{ln(0.925)} = 1 + \frac{2ln(0.925)}{ln(0.8)} = 1.7$$  \hspace{1cm} (34)$$

It allows finding minimal inversion (after generation of the Q-Switched pulse)

$$x = \frac{N_{min}}{N_{max}}$$ using following equation [37]:

$$1 - x - \frac{1}{r}ln\left(\frac{1}{x}\right) = 0$$  \hspace{1cm} (35)$$

This equation could be plotted and solved graphically from the Figure 34.
Figure 34. Plotted equation that gives the ratio of final to initial population inversion.

One can see from the figure that $x=0.3$ for the value of $r=1.7$. This graphical solution allows estimating $\frac{dN}{dt}$ from linear approximation as:

$$\frac{dN}{dt} = \frac{(N_{\text{max}} - N_{\text{min}})}{T_{\text{period}}} = (N_{\text{max}} - N_{\text{min}})f = (1 - 0.3)N_{\text{max}}f \approx 0.7N_{\text{th(n)}}f \quad (36)$$

Then the ratio of population inversion for current experimental conditions will be:

$$\frac{N_{\text{th(n)}}}{(dN/dt)} = \frac{1}{0.7f} = \frac{1}{0.7 \times 420 \text{Hz}} = 3.4 \text{ ms} \quad (37)$$

2.2.2.9. **Experimental Setup.**

Laser cavity configuration used for theoretical model verification is depicted in Figure 35. The 1.1 mm pump beam from the ELR-20-1532.6-LP fiber laser (IPG Photonics Corp.) is focused into the Er:YAG laser rod (0.25 % at. Er:YAG, 5 mm × 50 mm) through dichroic flat 45-degree folding mirror (FM) (HR@1600-1700 nm, AR@1532 nm) by a 300 mm AR-coated focusing lens (FL). The laser scheme
is based on a semi-concentric cavity design with the 250 mm end mirror and 80% output coupler (OC). Chromium doped ZnSe saturable absorber with initial transmission of 92.5% at 1645 nm was placed at Brewster angle 50 mm away from the dichroic mirror. Two laser resonators were investigated in this research: short cavity with a length of 142 mm and a long resonator with a length of 277 mm.

![Laser scheme for single mode measurements](image)

**Figure 35. Laser scheme for single mode measurements.**

**2.2.2.10. Experimental Results.**

Time resolved measurements of Q-switched pulse profile were performed for short and long cavities. A snapshot of the laser Q-switched pulse from the long cavity is shown in Figure 36a. As seen from the Figure 36a there is a strong longitudinal mode beating in a long cavity. Pulse duration in a 277 mm long laser cavity was approximately 80 ns. Pulse duration in a twice shorter cavity with a length of 142 mm was around 50 ns (Figure 36b). Comparing to long cavity in short resonator laser operates as predicted without mode beating in a single frequency regime.
Figure 36. Time resolved pulse profile in passively Q-switched regime: a) long cavity; b) short cavity.
It is noteworthy that it was difficult to estimate the pulse repetition rate due to a presence of a strong jitter. Pulse repetition rate jitter was measured using FSEA Spectrum Analyzer and is depicted in Figure 37. As one can see from Figure 37b, there is a strong instability in pulse repetition rate for a long cavity due to multimode operation and mode competition ($\Delta F_{r.r.}>170$ Hz at -10dB level). However, repetition rate for short cavity depicted in Figure 37a exhibits a rather small jitter ($\Delta F_{r.r.}<10$ Hz at -10dB level).

![Figure 37](image)

Figure 37. Pulse repetition rate jitter: a) short cavity, $L_{cav}=148$ mm; b) long cavity, $L_{cav}=278$ mm.

2.2.2.11 Conclusions.

Passive Q-Switching of Er-fiber-pumped Er:YAG hybrid laser was realized with the use of Cr:ZnSe saturable absorber. Single- and multi- longitudinal mode regimes of operation were analyzed experimentally and theoretically for different lengths of the cavities that did not contain additional mode selection elements. Theoretically and experimentally a single frequency regime of operation was realized for cavities and pump rates enabling difference in buildup time between two adjacent longitudinal modes.
greater than the pulse duration. For the same levels of output power the jitter in the pulse repetition rate was decreased by a factor of 17 reaching 2.5 % of operating frequency.

2.2.3. Actively Q-Switched Regime of Operation

The objective of this part of the work was to perform an investigation of performance of a fiber-bulk hybrid Er:YAG laser in acousto-optical Q-switched regime of operation with pulse repetition rate matching natural frequency of QTF of 32 kHz, and also sub-harmonic frequencies (8 kHz, 16 kHz).

2.2.3.1. Experimental Setup

An experimental setup depicted in Figure 38 was used to study active Q-Switching of the Er:YAG laser. The 1.1 mm pump beam from the ELR-20-1532.6-LP fiber laser (IPG Photonics Corp.) is focused into the Er:YAG laser rod (0.25 % at. Er:YAG, 5 mm × 50 mm) through dichroic flat 45-degree folding mirror (HR@1600-1700 nm, AR@1532 nm) by a 300 mm AR-coated focusing lens. The laser scheme is based on a semi-concentric cavity design with the 250 mm end mirror and 95 % output coupler.
2.2.3.2. Experimental Results

Experimental results for pumping power of about 11.5W are depicted in Table 5. One can see from the table that laser is capable of operation at repetition rates ranging from 100 Hz up to 63 kHz. However, output power, repetition rate, and pulse duration depend dramatically on the time of the AO Q-Switch opening (gate duration). The minimum time of the AO Q-Switch opening is limited to 0.5 μs by the Q-Switch driver. At this gate time the output pulse duration is about 40 ns. The data presented in Table 5 clearly shows that increasing of the AO Q-Switch gate opening time increases pulse duration.
Table 5. Output characteristics for Actively Q-Switched Er:YAG laser for pumping power of 11.5W

<table>
<thead>
<tr>
<th>Pump, W</th>
<th>ΔPump, μs</th>
<th>F, Hz</th>
<th>PRR, Hz</th>
<th>Pout, W</th>
<th>Δq-sw, ns</th>
<th>E, mJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-11.7</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>CW, 2.1-2.2</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>11-11.7</td>
<td>0.5</td>
<td>34.2k</td>
<td>34.2k</td>
<td>0.68</td>
<td>40</td>
<td>0.02</td>
</tr>
<tr>
<td>11-11.7</td>
<td>2.6</td>
<td>34.2k</td>
<td>17.1k</td>
<td>1.2</td>
<td>200</td>
<td>0.07</td>
</tr>
<tr>
<td>11-11.7</td>
<td>0.5</td>
<td>62.78k</td>
<td>62.78k</td>
<td>0.68</td>
<td>40</td>
<td>0.011</td>
</tr>
<tr>
<td>11-11.7</td>
<td>6.3</td>
<td>1k</td>
<td>1k</td>
<td>0.77</td>
<td>170</td>
<td>0.77</td>
</tr>
<tr>
<td>11-11.7</td>
<td>6.3</td>
<td>108.7</td>
<td>108.7</td>
<td>0.23</td>
<td>80</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Figure 39 depicts pulse profiles for 0.5 μs (left) and 2.6 μs (right) AO Q-Switch gate durations. It must be mentioned here that increasing the opening time will increase the output power, however, population inversion is not enough for every second pulse to oscillate and the laser tends to operate at half frequency of the AO Q-Switch driver settings. In these preliminary results we found experimentally that reflectivity of the output coupler of 95% creates a very high intra-cavity intensity causing optical damage of the cavity elements at pumping power levels above 12 W.
Figure 39 AO Q-Switched pulse profiles for AO modulation frequency of 34.2 kHz:
AO Q-Switch gate duration 0.5 μs (left) and 2.6 μs (right).

An output coupler of 95 % was replaced by 80 % reflectivity mirror to reduce intracavity intensity and avoid optical damage. Pumping lens was replaced by 200 mm focusing lens for best matching of cavity mode with pumping beam. Input – output characteristics were gathered at repetition rate of 8, 16, and 32 kHz for different AO gate durations over the range of available fiber laser pumping power. Dependences of the output power on pumping power for repetition rates of 8 and 16 kHz are depicted in the Figure 40.
Figure 40. Output power versus incident pumping power for different AO Q-Switch gate durations.

One can see from the graph that dependences have a similar trend with 20% lower output power for a higher repetition rate. Also reducing of the AO gate duration slightly reduces the output power. It must be mentioned here that at high AO Q-Switch repetition rates (i.e., 16 kHz and above) over the pumping interval the laser trends to operate on sub-harmonic AO frequencies having instability at some gate durations. Operation of the laser at 8 kHz of AO Q-Switch repetition rate was stable for all possible gate durations over the whole range of available pumping powers.

Input-output power dependence for a 32 kHz repetition rate for a number of selected AO gate durations is depicted in Figure 41. One can see from the graph that
shorter gate duration decreases the output power. However, at longest gate opening of 6.3 μs the laser output is similar to one in CW mode of operation (when AO Q-Switch is off, black curve). A purple curve on the graph corresponds to input-output power dependence for 8 kHz of repetition rate with 6.3 μs gate duration, and is depicted for comparison.

![Graph showing output power versus incident pumping power for different AO gate durations at 32 kHz AO Q-Switch repetition rate.](image)

**Figure 41.** Output power versus incident pumping power for different AO gate durations at 32 kHz AO Q-Switch repetition rate.

Stability of the output lasing for 32 kHz repetition rate versus AO gate duration for 16 W of pumping power is depicted in Figure 42. One can see from the figure that there is a stable operation of the laser at original and sub harmonic AO Q-Switch frequencies corresponding to a particular AO Q-Switch gate duration ranges. Gray area in
the figure represents an unstable region when laser operates on more than one sub-harmonic. Output lasing for 32 kHz AO Q-Switch modulation was found to be stable at gate duration below 0.6 μs. Thus, this data demonstrates a capability of the developed laser to operate in the regime matching required conditions of a pump source for QEPAS detection platform.

**Figure 42.** Output lasing stability for 32 kHz repetition rate versus AO gate duration for 16 W of pumping power.
CHAPTER III

SINGLE FREQUENCY BROADBAND Cr\textsuperscript{2+} DOPED ZnS LASER WITH A FINE TUNING

3.1 Introduction

Chromium doped zinc selenide active crystals (AC) proved [17] to be effective sources of coherent radiation in 2-3 \( \mu \)m spectral region under 1.5-2.1 \( \mu \)m excitation. Lasers based on this AC can operate in free running mode as well as in selective regime with fine tuning of output radiation [17]. Output powers exceeding 10 W and efficiency up to 70\% have been demonstrated [17,18,19,20] in several Cr doped semiconductors, making these materials ideal candidates for mid-IR tunable laser systems.

The main objective in this part of the thesis is to realize single frequency operation on chromium transitions with output laser parameters suitable for QEPAS detector as part of the “Optical Nose” platform. Since the resonant frequency of the QEPAS detector is 32 kHz there are two scenarios to achieve the above objectives:

- Gain-switched mode of operation with precise stability of pulse repetition rate at 32 kHz and at sub harmonic QTF natural frequencies at 16 kHz and 8 kHz.
- CW mode of operation with laser output wavelength modulation with frequency of 16 kHz.
3.2 Gain-Switched Lasing

3.2.1 Pumping by Passively Q-Switched Lasers

Passively Q-Switched lasers described in chapter 2 have a number of advantages including simplicity, compactness, and inexpensive design. Ability to operate at few kilohertz of pulse repetition rate with millijoule level of output energy makes them a reasonable pumping sources for the mid-IR lasers based on \( \text{Cr}^{2+}:\text{ZnSe}/\text{ZnS} \) active crystals. Absorption cross-section of the chromium ions in ZnSe host has a maximum at 1.77 \( \mu \text{m} \). Because of that Er:YAG laser with output radiation of 1645 nm is more efficient pumping source with respect to Ho:YAG laser operating at 2.1 \( \mu \text{m} \) (see Figure 5). Tunable, compact, simple in design mid-IR \( \text{Cr}^{2+}:\text{ZnSe} \) laser source operating at 32 kHz (and/or 16 kHz, 8 kHz) would be very beneficial for QEPAS applications. The experimental setup depicted on Figure 43 was assembled to study \( \text{Cr}^{2+}:\text{ZnS} \) laser under passively Q-Switched Er:YAG laser excitation in non-selective cavity.

![Passively Q-Switched Er:YAG laser 32, 16 or 8kHz](image)

Figure 43. Nonselective optical scheme of a gain-switched Cr:ZnS laser.

It was difficult to realize passively Q-Switched operation of the Er:YAG laser at high repetition rates (i.e. 32 kHz, 16 kHz, and other sub harmonic frequencies of QTF) with good stability and small jitter. Power stability and absence of the jitter is a major requirement for QEPAS detection system.
3.2.2 **Pumping by Actively Q-Switched Er:YAG Laser**

An actively Q-Switched Er:YAG laser modulated at 32 kHz was used as a pumping source for studying gain-switched mode of operation of Cr:ZnS laser in a non-selective cavity. Output gain switched pulse profile and pumping pulse are depicted in Figure 44.

![Cr:ZnS gain-switched pulse duration](image)

**Figure 44.** Pump and Cr:ZnS gain-switched pulse profiles.

Trains of output Cr:ZnS gain-switched output pulses and pumping pulses are depicted in Figure 45 and Figure 46, respectively.
Figure 45. Train of Cr:ZnS gain-switched output pulses at 32 kHz.

Figure 46. Train of the AO Q-Switched Er:YAG pumping pulses at 32 kHz.
Gain-switched pulse starts to generate during pumping pulse without a noticeable delay on the measured timescale, and the output repetition rate perfectly matches the pumping one.

It is known that pulse to pulse jitter of the actively Q-Switched lasers is very small. It is interesting to verify if the jitter of the Cr:ZnS laser pumped by AO Q-Switched Er:YAG laser will be also negligible for QEPAS applications. A Littman resonator configuration (see Figure 47) was used to investigate single frequency regime of Cr:ZnS laser operation with fine tuning capability.

Figure 47. Optical scheme of a gain-switched Cr:ZnSe laser (Littman configuration).

It is believed that QEPAS technique is sensitive not only at 32 kHz of pulse repetition rate but at sub harmonics frequencies (i.e. 16 kHz, 8 kHz) also. Study of the gain-switched Cr:ZnSe laser pumped by actively Q-Switched Er:YAG laser results in the following conclusions:

a) Cr:ZnSe laser capable to operate in gain-switched regime at pulse repetition rate matching resonant frequency of quartz tuning fork of 32 kHz and on its sub harmonics (16 kHz, 8 kHz) with good pulse-to-pulse stability (see Figure 46 as an example).
b) Limited duty-cycle range of the actively Q-Switched Er:YAG laser operating at repetition rate matching resonant frequency of quartz tuning fork of 32 kHz and on its sub harmonics (16 kHz, 8 kHz) results in spectral instability of Cr:ZnS gain-switch laser operation such as multimode regime.

c) The conclusion above gives hope of finding optimized parameters of duty-cycle and modulation depth of the other pumping sources which could result in stable wavelength modulation of the Cr:ZnS laser emission.

3.3 CW Broadly Tunable Cr\textsuperscript{2+}:ZnS/Se Laser With Wavelength Modulation at 16 kHz

3.3.1 Introduction

Sensitivity of the QEPAS detector depends on the absorption rate which should match resonant frequency of the QTF. It could be realized by modulation of the lasing wavelength at a one half of QTF natural resonant frequency. In this case, the shock wave from the absorbed energy of the laser emission occurs twice during one period of the modulated laser wavelength.

The schematic diagram for Cr:ZnSe/ZnS single frequency laser is shown in the next Figure 48, where Fp is pumping focusing lens; IM is input mirror; FC is intracavity lens; Gr is diffraction grating (600 gr/mm); BM is back mirror.
In our experiments in this part of the work we used polycrystalline Cr:ZnS active crystal (2.02 x 5.05 x 9.04 mm) with AR coating on both facets of 2x5 mm and chromium concentration of 9.64x10^{18} \text{ cm}^{-3}. The reflection of multilayer coating was less than 1% at pumping wavelength of 1.5 \mu\text{m} up to 3 \mu\text{m}.

To realize single frequency oscillation the incident angle was adjusted between 84^\circ and 89^\circ. Usually, the tuning of the lasing wavelength could be achieved by rotation of the back mirror. To demonstrate tuning over 2-3 \mu\text{m} spectral range with 600 gr/mm grating, the back mirror should be rotated over the angle range of \Delta\phi=41^\circ. Figure 49 shows tuning dependence for Cr:ZnSe laser for 88^\circ of incident angle (red curve).
Figure 49. Tuning dependence for the laser for angle of incidence of $88^\circ$ (red curve). Blue curve is tuning dependence for autocollimation regime.

Zero order of diffraction was used for radiation output. In this configuration the direction of the output beam does not depend on oscillation wavelength which could be calculated using classical diffraction grating equation:

$$d \left( \sin(\theta_i) + \sin(\theta_d) \right) = m\lambda \quad (3.1)$$

Where $\theta_i$ is grazing incident angle; $\theta_d$ is angle of diffraction; $d$ is a grating period; $m$ is integer; $\lambda$ is wavelength.

It is important to note that additional “ghost” lasing condition could prevent tunable lasing at short wavelengths. The ray diagram for this condition is shown in Figure
50 by green rays. This condition could have happened when beam reflected from the BM satisfies the auto-collimation regime: angle of incidence equals to the angle of diffraction:

\[ 2d \sin(\theta_a) = m\lambda \]  \hspace{1cm} (3.2)

where \( \theta_a \) is an angle of the auto-collimation regime.

![Ray diagram of diffraction grating operation in Littman cavity configuration (red) and Littrow autocolimation regime (green).](image)

The tuning curve for this lasing condition is shown in the Figure 49 by blue curve. As one can see from the Figure 49 the lasing oscillation at 2.25 \( \mu \)m can be accompanied by lasing at \( \sim 2.65 \) \( \mu \)m in the auto-collimation condition. It could be suppressed by the use of appropriate aperture. It is difficult to demonstrate fast scanning of the oscillation wavelength by BM due to its large aperture and mass. However limited fast scanning
range could be realized by parallel shift of the IM. In this case tuning range will be limited by the cavity free spectral range \( \Delta v = \frac{1}{2L_{cav}} \) and could be achieved by parallel shift of the input mirror by a distance of \( \lambda/2 \).

For the typical Cr\(^{2+}\):ZnS laser cavity lengths of 15cm the free spectral range is:

\[
\Delta v_{nm} = \frac{1}{2L_{cav}} = \frac{1}{2 \times 15cm} = 0.033 \text{ cm}^{-1} = 1\text{GHz} \approx 0.02nm@2.4\mu m. \tag{3.3}
\]

Thus, due to a small aperture of the IM the mechanical resonance of the tuning mechanism could be very high (~100 kHz) allowing rapid tuning within 20 pm wavelength range.

There are other physical mechanisms which could be used for rapid scanning of the oscillation wavelength. The first mechanism is a modulation of the pump intensity. Using external modulator based on acousto-optical devices the maximum modulation frequency is limited by sound propagation across pumping beam. Using acoustic velocity of 5.96 km/s in the fused silica and ~1 mm beam diameter the maximum modulation frequency could be estimated as ~6 MHz. There are several physical reasons which could result in frequency modulation of the Cr:ZnS lasing under pump intensity modulation. First reason is dependence of the gain cross section on inversion in the gain element. Due to overlap absorption and emission cross-section (see Figure 51a) the total gain cross-section could be calculated using following equation:

\[
\sigma_g(\lambda) = n_2\sigma_{em}(\lambda) - (1 - n_2)\sigma_{ab}(\lambda), \tag{3.4}
\]

Where \( n_2 \) is a relative population of the upper laser level. The calculated spectra of the gain cross-sections for different \( n_2 \) are shown in Figure 51b.
As one can see from the Figure 51 the shape of the gain cross-section depends on upper laser level population. To estimate spectral dependence of the lasing wavelength due to this effect, we will consider normalized gain spectra. The resolving power of the grating is $R=q*N$, where $q$ is diffraction order and $N$ is the total number of grooves illuminated on the surface of the grating. For 2 cm beam diameter, and grating with 600 gr/mm, the resolving power of the grating could be calculated as $R=12000$ for the first order of diffraction. The black curve in the Figure 52A shows normalized spectral shape $g_{Gr}(\lambda)$ of the grating selector after a round trip of the radiation in the cavity. The spectral dependence of the gain cross-section will results in different shift of the maxima of the cavity form-factor shape. The colored curves (see Figure 52) show this dependence for the oscillation wavelength near 2.35 $\mu$m. As one can see from the figure, the maximum
shift corresponds to the minimum inversion in the gain element. Dependence of the position of the maxima on the inversion in the gain element is depicted in Figure 52B. From this estimation we can conclude that only 100-200 MHz shift could be achieved due to this effect.

Figure 52. A) Gain cross-section profile shifts (colored curves) for different upper laser level population operating near 2.35μm and normalized gain spectral shape (black curve); B) Position of the gain maxima vs relative population of the upper laser level in the AC.
Thermal effect could be involved as an additional frequency shift from the pump modulation. It will result in increase of the effective cavity length ($L_{\text{eff}}$) due to thermo-optical effect:

$$L_{\text{eff}} = L_{\text{air}} + nL_{\text{gain}}, \quad (3.5)$$

Where $L_{\text{air}}$ – cavity propagation length in the air; $L_{\text{gain}}$ – length of the gain element; $n$ – is a refractive index of the active crystal ($n=2.44$ for ZnSe). As one can easy estimate for cylindrical symmetry, with homogeneously distributed heating source $q_0$ [W/cm²·cm] within radius $r_0$, the temperature change at the edge of the pump area will be

$$\Delta T_0 = \frac{q_0 r_0^2}{4\chi}, \quad (3.6)$$

Where $\chi=0.17$ W/cmK is a thermal conductivity of the ZnSe. For the total heating power $P_h$ in the crystal of length $L_{\text{gain}}$, the absorbed distributed heating source will be

$$q_0 = \frac{P_h}{\pi r_0^2 L_{\text{gain}}}, \quad (3.7)$$

Then we can estimate temperature change as:

$$\Delta T_0 = \frac{q_0 r_0^2}{4\chi} = \frac{P_h}{4\pi \chi L_{\text{gain}}}, \quad (3.8)$$

For the total heating power $P_h=4$W in the crystal length $L_{\text{gain}}=0.4$ cm, the temperature change will be:

$$\Delta T_0 = \frac{4W}{4\pi \chi 0.17 \frac{W}{\text{cmK}} 0.4 \text{ cm}} = 4.7K, \quad (3.9)$$

This temperature will enable a decrease of the cavity length on:
\[ \Delta L_{\text{cav}} = L_{\text{gain}}(n + \Delta n) - L_{\text{gain}}n = L_{\text{gain}} \left( \frac{dn}{dT} \right) \Delta T = 0.4 \, \text{cm} \left( 6.5 \times 10^{-5} K^{-1} \right) 4.7K = 1.2 \, \mu m, \quad (3.10) \]

To obtain oscillation wavelength on cavity free spectral range, the change of the cavity length \( \Delta L_{\text{cav}} \) should be equal to \( \lambda/2 \), which corresponds to modulation of the heating power \( \Delta P_h \sim 4 \, \text{W} \) for \( \lambda = 2.4 \, \mu m \).

In case of Cr:ZnS lasers the following constants used in calculations:

- Refractive index: \( n = 2.26 \) at 2.4 \( \mu m \)
- Thermal conductivity: \( \chi = 0.272 \, \text{W/cmK} \)
- Thermal Coefficient of Refractive Index: \( \frac{dn}{dT} = 4 \times 10^{-5} K^{-1} \)

\[ \Delta n = \left( \frac{dn}{dT} \right) \Delta T, \quad (3.11) \]

\[ \Delta L_{\text{cav}} = L_{\text{gain}} \Delta n = L_{\text{gain}} \left( \frac{dn}{dT} \right) \Delta T = \frac{dn}{dT} \frac{P_h}{4\pi \chi} = \frac{4W}{4\pi \cdot 0.27} (4 \times 10^{-5} K^{-1}) = 0.468 \, \mu m, \quad (3.12) \]

This is about 2.5 times smaller than 1.2 \( \mu m \). Thus, to realize wavelength modulation within laser cavity free spectral range a modulation of 10 W of the pumping power should be implemented.
3.3.2 Tunable Hybrid Fiber-Bulk Cr:ZnS Laser With Wavelength Modulation by Modulated Pumping Power.

Middle Infrared spectral region contains strong absorption lines of the most of organic molecules, and coincides with transparency window of the atmosphere. Spectroscopic applications such as quality control, materials characterizations, pollution monitoring would be more advanced with the use of Mid-IR laser sources while techniques used in other spectral regions are not efficient or absent at all. Recently discovered transition metal doped II-IV chalcogenide laser materials proved its feasibility and high quality of operation in Mid-IR spectral region as an effective saturable absorbers and more importantly as an active crystals for new type of inexpensive solid state laser sources.

As an alternative way concluded in a previous paragraph there is a possibility to realize wavelength modulation by modulated pumping power at duty cycle and modulation depth just enough to tune the wavelength within the spectral range of the Cr:ZnS laser cavity.

A laser system described here is based on a hybrid-fiber-bulk approach with the use of polycrystalline Cr:ZnS crystal as a gain element and Littman-Metcalf mode-hop free tunable cavity design.

The experimental setup used to investigate input-output power characteristics and spectral tunability parameters is depicted in Figure 53.
Figure 53. Experimental setup of Tunable Hybrid Fiber-Bulk Cr:ZnS Laser with a wavelength modulation.
The 1.1 mm pump beam from the ELR-20-1532.6-LP fiber laser (IPG Photonics Corp.) is focused into the Cr:ZnS laser gain element \( (N_{\text{Cr}}=4.74 \times 10^{18} \text{ cm}^{-3}) \) by a pumping lens (\( f=25 \text{ mm} \), antireflection coated at pumping wavelength) through a dichroic pumping mirror (HR@1900-3200 nm, AR@1532 nm). Cr:ZnS active crystal is installed in the conductively cooled copper jacket and is maintained at room temperature. A Littman-Metcalf mode-hop free tunable cavity scheme implemented in the setup to investigate wavelength tunability characteristics consists of the diffraction grating (600 gr/mm) installed at grazing incidence (88º), which position is fixed, high reflection silver rotating mirror, and intracavity lens (\( f=20 \text{ mm} \), AR@2-3 μ). Efficiency of the diffraction grating at a grazing incidence is around 85 % which makes an output lasing from 0th order very useful for measurements since there is no lateral beam displacement. Output spectral characteristics were monitored with the use of EXFO WA-1500 Spectrum Analyzer with combination of USB-controlled EXFO WA-650 Wavemeter for measuring precisely (60 MHz resolution at wavelength of 1 μ) laser wavelength and ThorLabs TL-15 Interferometer for tracking laser output features and linewidth measurements.

A moderate pumping power of 10 Watt efficient for stable operation of the laser scheme described was used to analyze the range of tunability of the hybrid fiber-bulk Cr:ZnS laser setup depicted in Figure 53. Output laser power measured for spectral region 1950-2500 nm is depicted in Figure 54.
The laser wavelengths were measured with EXFO WA-1500 Spectrum Analyzer - EXFO WA-650 Wavemeter tandem. The linewidth of the output lasing was measured with ThorLabs TL-15 Interferometer with a free spectral range (FSR) of 15 GHz. The maximum finesse of the interferometer is 150 and corresponds to the 2.4-2.5 μm spectral range, gaining the best resolution of ~ 100MHz. Here must be mentioned that finesse of the interferometer is very sensitive to the alignment and could decrease the resolving power of the interferometer. Linewidth measurements at wavelength below 2.4 μm have lower spectral resolution. Cr:ZnS laser was adjusted to 2.4 μm for maximum resolution.
of the interferometer to characterize power dependence of the laser linewidth for the range of available pumping power. The desired laser wavelength was monitored with EXFO WA-1500 Spectrum Analyzer -EXFO WA-650 Wavemeter tandem is depicted in Figure 55.

![Figure 55. Single line of Cr:ZnS laser at 10 W of pumping power.](image)

An output power and linewidth of Cr:ZnS laser tuned to 2.4 μm measured for the whole range of the available pumping powers are depicted in Figure 56.
One can see from the graph above that linewidths of the Cr:ZnS laser output emission lie within 350-420 MHz for the whole range of the pumping powers. It must be mentioned here that the laser output spectra experienced instabilities at threshold conditions as well at maximum incident power. Stable parameters were observed in the range of 7-12 W, which are typical pumping powers for such lasers. Slight variations of laser linewidths in this range are due to individual cavity parameters at different values of pumping powers and are caused by thermal lensing effect in active crystal. The linewidth of the output lasing were measured with ThorLabs TL-15 Interferometer.
signal for single-frequency Cr:ZnS laser operating around 2404 nm at 10 W of pumping power is depicted in Figure 57.

![Interferometer scan of 2404 nm Cr:ZnS laser emission](image)

**Figure 57.** Interferometer scan of Cr:ZnS laser emission at 2404 nm.

A red curve in the Figure 57 represents a ramp voltage applied to the piezoelectric actuator with one of the interferometer’s cavity mirror attached to it. Displacement of the mirror defines standing wave in the cavity of the interferometer. Half wavelength displacement of the mirror allows observing spectral composition of the laser emission within 15 GHz frequency range. In the figure above a black curve corresponds to the interferometer transmission. One can see from the figure that Cr:ZnS laser operating at 2404 nm wavelength has no spectral artifacts between two cavity modes. This result is a
prove of a single frequency of Cr:ZnS laser operation. A more detailed spectral profile is depicted in Figure 58.

![Spectral profile of the Cr:ZnS laser tuned to 2404 nm](image)

Figure 58. Spectral profile of the laser emission line at 2404 nm.

One can see from the figure that the laser emission linewidth is $\Delta \nu = 355$ MHz (at FWHM) and has a spectral purity preferred for the most spectroscopic applications.

A Cr:ZnS laser was adjusted to operate at 2470 nm wavelength to estimate accuracy of the linewidth measurements. Input-output characteristics of the Cr:ZnS single frequency laser tuned to 2470 nm is depicted in Figure 59.
One can see from the figure that the linewidth of the laser emission lies within 340-400 MHz frequency range. Spectral profile of the laser line emission at 11.6 W of pumping power is depicted in the Figure 60.
Figure 60. Spectral profile of Cr:ZnS laser emission line at 2470 nm.

Figure above illustrates Cr:ZnS laser emission line profile of a good spectral purity which is similar to spectral profiles and linewidths measured inside 2.4-2.5 μm spectral region. The strongest absorption lines of the NH$_3$ molecules overlapping with Cr:ZnS emission correspond to the spectral region around 2.3 μm. Similarity in a spectral profiles of Cr:ZnS laser emission lines in the 2.4-2.5 μm spectral region suggests that emission at 2.3 μm would have the similar trend.

The major issue the laser based spectroscopic techniques relates to is inability of fine tuning and/or wavelength modulation of the laser radiation. Sensitivity of the
detection of the sample could be dramatically increased with the help of a QEPAS technique. QEPAS requires wavelength modulation and tunability around absorption lines of the analyzed species. This part of the work is devoted to investigation of the possibility of the Cr:ZnS laser output wavelength modulation. It was suggested in the previous section that the laser wavelength could experience modulation with power modulation of a pumping source. A depth of modulation was investigated to realize conditions of wavelength modulation.

A modulated signal was provided to the analog input of the Er-fiber laser by a Stanford Research Function Generator model DS345. This generator is capable of providing triangle shape wave function. Such dynamics is preferred for applications in temporal domain where a tuning wavelength should remain at constant speed. A modulated output power was measured for frequency range up to 16 kHz. The depth of modulation of Cr:ZnS laser (blue curve) and pumping source (black curve) is depicted in Figure 61. One can see from the figure that the depth of erbium fiber laser modulation drops down a factor of four from 1Hz up to the 16 kHz of modulation frequency. It must be mentioned here that while fiber laser analog circuit being not designed to process fast signals it is still capable of modulation at 16 kHz required for QEPAS detection system. The depth of modulation of the Cr:ZnS laser was measured for the same frequency range as for the erbium fiber laser. The modulation depth of the Cr:ZnS laser drops down to a factor of five at high frequencies of 16kHz.
Figure 61. Modulation depth of the Cr:ZnS laser (blue curve) and pumping source (black curve).

The maximum scan frequency of the interferometer is 50 Hz which makes it difficult to monitor spectral features at higher frequency. A 0.1 Hz frequency was chosen to investigate wavelength modulation by modulated pumping power. A position of the laser emission line was monitored with the interferometer and is depicted in Figure 62.
Figure 62. Range of Cr:ZnS emission wavelength modulation by pumping power.

One can see from the Figure 62 that changing pumping power from 9.5 W up to 11.1 W causes smooth frequency shift of the laser line by 0.5 GHz. It must be mentioned here that, as was described in the introduction section of this chapter, two scenarios could be involved in laser emission line frequency shift by modulating of pumping power. The first one is devoted to modulation of the gain with the pumping power and can allow shifting the laser frequency by 200 MHz. The other explanation of the frequency displacement is a thermo optical effect.
However, in this experiment a smooth frequency shift was observed without jumping from one longitudinal mode to another. This can be explained by the thermal effects only, since the gain modulation suggests cavity modes to be fixed to its fixed cavity length but shifted gain should select emission to a stronger cavity mode. In this case the tuning of the laser could looks like switching from one cavity mode to the next one in a discrete order which is opposite to the observed continuous shift.

3.3.3 Wavelength Modulation by Mirror Displacement.

In this part of the work we utilized NOLIAC piezoelectric actuator (Model #NAC2011) as an active mirror displacement element. The maximum displacement of 3μm could be achieved at applied maximum allowed voltage of 150V. An epoxy was used to glue one side of the actuator to the ultrafast pumping mirror (HR@1900-3200 nm, AR@1532 nm). Another actuator was glued to the Newport X-Y adjustable mirror holder. A Stanford Research Function Generator model DS345 was utilized as a driver for piezoelectric actuator. The maximum available voltage the generator can supply is 10 V making it to achieve mirror displacement of 200 nm. An experimental setup we implement in this part of research is depicted in Figure 63.
Figure 63. Schematic diagram of CW Single-Frequency Cr:ZnS laser with modulated wavelength at 16 kHz.

Output spectral characteristics were monitored with the use of EXFO WA-650 Wavemeter for wavelength measurements of the laser emission and ThorLabs TL-15 Interferometer for tracking laser output spectral features and linewidth recording. Scanning frequency of the interferometer is 50 Hz which puts a limitation on laser spectral line measurements at higher modulation rates. In our experiments we used a slow repetition rate of 0.1 Hz to analyze tunability of the laser line by mirror displacement. The experimental setup used in this part of the work is similar to the one investigated in the previous chapter (see Figure 53) with cavity length shortened by 75mm to increase a free spectral range of the laser cavity, which in turn, will increase the range of tunability at 200 nm mirror displacement with respect to a longer laser cavity scheme.

The results on wavelength tunability by mirror displacement are depicted in Figure 64. One can see from Figure 64 8.9V applied voltage to the actuator results in a laser line frequency shift of 170MHz. A good repetitiveness of the results obtained
suggests that this is a method of choice to realize Cr:ZnS wavelength modulation required for QEPAS platform to operate.

Figure 64. Cr:ZnS laser emission line wavelength modulation via mirror displacement.

A range of PZT actuator extension with applied voltage could be limited by the soldered electrodes and residue of the epoxy glue preventing it to achieve full stroke extension at maximum allowed voltage of 150V. A Tektronix PS280 DC Power Supply with variable output DC voltage from 0 up to 60V was utilized to investigate Cr:ZnS laser emission line frequency tuning range by mirror displacement at longer distances.
The experimental setup as on Figure 63 was used to perform these measurements at 10W of incident pumping power. The Cr:ZnS laser emission line frequency was tuned to 2400nm. The output power of 0.7W from Cr:ZnS single mode laser remained constant and stable during the experiment. The emission line frequency shift of the Cr:ZnS laser for 0-60V range of applied actuator voltage is depicted in Figure 65.

Figure 65. Cr:ZnS laser emission line frequency shift for different mirror displacement actuator voltages.

One can see from the figure that Cr:ZnS laser emission line has similar intensity at different applied actuator displacement voltage and the same linewidth of 375 MHz.
Cr:ZnS laser emission line frequency shift as a function of mirror displacement actuator voltage is depicted in Figure 66.

![Graph](image)

**Figure 66.** Cr:ZnS laser emission line frequency tuning as a function of applied displacement voltage.

One can see from the figure above that Cr:ZnS laser emission line frequency tuning shows near linear dependence with applied voltage on the mirror displacement actuator. Linearity of the frequency tuning is a crucial factor for QEPAS technique since the resonance conditions on which those systems are based are phase dependent. Analysis of the data obtained shows that the laser exhibits good stability of operation over the whole range of wavelength tunability.
As a result of this work we realized optimized conditions of CW Erbium fiber laser pumped Single Frequency Cr\textsuperscript{2+}:ZnS laser operation with simultaneous broad mid-IR wavelength tuning and wavelength modulation at 16 kHz or other sub harmonic frequencies of QTF (i.e. 8,4,2 kHz) within a free spectral range of a cavity.
CHAPTER IV

DEMONSTRATION OF ORGANIC MOLECULAR TRACE-GAS DETECTION IN THE MULTI-PASS CELL USING DEVELOPED TUNABLE MID-IR LASER SOURCE.

4.1 Introduction

Alkanes such as ethane are believed to be markers of lipid peroxidation and have been demonstrated in a variety of pathological conditions. Elevated breath ethane was observed after ischemia/reperfusion [38], alcohol abuse [39], and patients with chronic pulmonary diseases. Many lung disease including chronic obstructive pulmonary disease, asthma, bronchiectasis, cystic fibrosis, interstitial lung disease, and acute respiratory distress syndrome are linked to chronic or acute inflammation. Because peroxidation is a basic mechanism of inflammatory process, organic lipid peroxidation markers should be found elevated under this conditions. Ethane level is increased in patients with asthma [40,41], chronic obstructive pulmonary disease (COPD) [42], obstructive sleep apnea [43], and acute respiratory distress syndrome (ARDS) [44].

The characteristic odor of uremic breath due to elevated levels of dimethylamine and trimethylamine has been known for a long time. Previously, amines were identified and quantified in human breath [45]. Considerable level of ammonia in the blood will appear if removal through conversion to urea is limited due to an impairment of liver function. Ammonia could also be identified in the breath of uremic patients [46].
4.2 Experimental Setup

The optical nose system (see Figure 67) consists of CW Cr:ZnSe laser operating in single longitudinal mode (SLM) rapidly-tunable in 2.2-2.7 μm spectral region, Astigmatic mirror multi-pass IR absorption cell (AMAC-200, Aerodyne Research, Inc.) with 210 m optical pass and detection system based on InGaAs detectors with low noise pre-amplifiers and a digital oscilloscope (Tektronix, TDS5104, 1GHz sampling rate).

The design of multi-pass optical cell is based on configuration presented by Herriott and coworkers [47,48] and described in details by McManus, et al. [49]. Briefly, the basic Herriott cell, also known as an off-axis resonator, consists of two spherical mirrors separated by roughly their radius of curvature. The laser beam is injected through a hole in entrance mirror in an off-axis direction, and recoils 238 times before exiting through the coupling hole. The beam path length can be changed by adjusting mirror separation. The beam spots fall on elliptical patterns on the mirrors, and the beam fills volume of the cell with the shape of a flattened hollow hyperboloid. The laser beam exits the cell at an angle from the input direction, and the cell can be treated simply as an optical element equivalent to a reflection from a convex mirror in the position of the coupling hole.

The CW Cr$^{2+}$.ZnSe SLM laser is based on a modified Kogelnik/Littman cavity shown schematically in Figure 67. The cavity consists of 25 mm radius of curvature (ROC) input mirror, 50 mm ROC folding mirror (both of which are AR/HR coated at 1.56 μm/2.0-3.0 μm, respectively), a highly efficient (50% into the 1st order at 75° incident angle) gold-coated reflective diffraction grating (600 grooves per mm), and a flat tuning mirror, mounted on motorized rotational stage for coarse wavelength scanning accompanied by a piezo-driven mirror shaker for the fine wavelength scanning. The
A motorized rotational stage allows scanning in the 2200-2550 nm spectral range at 3.5 nm/s rate, the shaker allows fine 2 nm wide mode hop free wavelength scanning at a rate ≤1 Hz. The multi-crystalline 1.5 mm long Cr$^{2+}$:ZnSe gain element, installed in the laser cavity at the Brewster angle for horizontal polarization, is mounted on a thermo-electrically/air cooled (TEC) copper block for thermal stabilization. The fine spectral structure of the laser output radiation, acquired with a scanning Fabry-Perot interferometer (FPI), is shown in Figure 68. The measured FPI finesse is about 7.3 and its base is 160 mm (while the SLM laser optical length is 100 mm), and thus the 120 MHz linewidth is an upper estimate limited by the interferometer spectral resolution. The laser delivers 150 mW output power at 6 W pump in the SLM regime of operation, which corresponds to 2.5% real optical efficiency and limited mostly by inadequate efficiency of the Littman grating.

![Experimental setup](image)

Figure 67. Experimental setup.
Figure 68. The fine structure of the laser output spectrum obtained with an FPI demonstrating \( \approx 120 \) MHz laser linewidth.

The noise level of the detection system was measured with an optical cell evacuated to \( 10^{-6} \) Torr pressure. The laser wavelength was set to 2445.96 nm and wavelength scanning was disabled. The noise signal shown in Figure 69 has 3\( \sigma \) level at 0.378 mV.
4.3 Results

The system operating in coarse scanning mode allows rapid wavelength tuning from 2200 nm to 2550 nm at a rate 3.5 nm/s. However, at the moment the laser is not operating in a SLM regime due to mechanical walk-off of the rotational stage and the mode hopping when rotational stage is used. The SLM regime of operation was available using piezo-driven mirror shaker designed for the fine wavelength scanning. We were able to record only low resolution absorption spectra of ethane and ammonia in wide 2200-2550 nm spectral region, as shown in Figure 70a and Figure 71a. The corresponding IR absorption spectra of ethane and ammonia obtained from Pacific
Northwest National Lab (PNNL) [50, 51] are shown in Figure 70b and Figure 71b, respectively.

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Figure 70. Low resolution absorption spectra of ethane a) obtained in coarse mode of operation, b) obtained from Pacific Northwest National Lab (PNNL) database [50, 51].
We were able to record high resolution spectra by using piezo-driven mirror shaker, as was described previously in experimental setup section. This regime of operation is allowing scanning in relatively narrow spectral window, i.e. 2 nm. The Cr$^{2+}$:ZnSe laser was operating mode hope free in SLM regime with a laser linewidth $\leq$120 MHz, as shown in Figure 68. In contrast to the coarse mode of operation, ethane absorption lines were well resolved in 2.2-2.6 $\mu$m spectral region and one of the
strongest absorption bands of ethane at 2446.12 nm is shown in Figure 70a. The pressure of ethane in the multi-pass cell was $4 \cdot 10^{-2}$ Torr, which corresponds to 52.6 ppmv under ambient conditions. The sensitivity of the system was estimated by comparing signals when laser wavelength was tuned in resonance with ethane absorption and tuned off resonance, i.e 2446.12 nm and 2445.93 nm respectively, as shown in Figure 72b and c. The signal difference between on and off resonance was equal to 3.72 V. Taking in to account noise signal, one can find the signal to noise ratio (SNR) equal to 29524 and the $3\sigma$ sensitivity level equal to 5 ppbv.

Similar results were obtained in the case of ammonia measurement. The one of the strongest absorption band of ammonia at 2296.45 nm is shown in Figure 73a. Ammonia concentration was equivalent to 448 ppbv during these measurements. The sensitivity of the system was estimated by the comparison of signals when laser wavelength was tuned in resonance with ethane absorption and tuned off resonance, i.e 2296.45 nm and 2296.68 nm, as shown in Figure 73 c and b. The signal difference between on and off resonance wavelength was equal to 1.56 V. Taking in to account noise signal, one can find the signal to noise ratio (SNR) equal to 12381 and the $3\sigma$ sensitivity level equal to 0.11 ppbv.

The chemical materials used in the experiment Ethane Assay $\geq 99.95$ (GC) was purchased from Fluka Analytical and Ammonium hydroxyde 5.0 N solution in water was purchased from Sigma Aldrich.
Figure 72. High resolution spectra of ethane a) transmission, b) signal level off resonance and c) signal level at resonance.

Figure 73. High resolution spectra of ammonia a) transmission, b) signal level off resonance and c) signal level at resonance.
CHAPTER V

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

1) A development of compact and efficient passively and actively Q-switched Tm-fiber-Ho:YAG, hybrid laser reported. For the cavity optimized at high repetition rate, the laser efficiencies of the free-running CW and fused silica acousto-optical actively Q-switched operation modes were equal to each other and exceeded 50%. An output energy as high as 15 mJ at 100 Hz repetition rate was demonstrated for the cavity optimized for low preparation rate. It was shown that Cr:ZnSe crystals are efficient passive Q-switches for the cavities of Ho:YAG laser. A single frequency regime of Ho:YAG lasing was achieved in Cr:ZnSe passive Q-switched regime of operation without any additional intracavity selective elements. The maximum output energy of 3 mJ was achieved in the passively Q-switched Ho:YAG laser cavity with efficiency as high as 84% with respect to free-running CW laser efficiency.

2) Passive Q-Switching of Er-fiber-pumped Er:YAG fiber-bulk hybrid laser was realized with the use of Co:ZnS and Cr:ZnSe saturable absorbers. Single- and multi- longitudinal mode regimes of operation were analyzed experimentally and theoretically for different lengths of the cavities that did not contain additional mode selection elements.

3) Theoretically and experimentally a single frequency regime of operation was realized for cavities and pump rates enabling difference in build-up time between
two adjacent longitudinal modes greater than the pulse duration. For the same levels of output power the jitter in the pulse repetition rate was decreased by a factor of 17 reaching 2.5% of operating frequency.

4) Cr:ZnSe laser capable to operate in gain-switched regime at pulse repetition rate matching resonant frequency of quartz tuning fork of 32 kHz and on its sub harmonics (16, 8 kHz) with good pulse-to-pulse stability was developed.

5) Cr:ZnS and Cr:ZnSe CW tunable single frequency solid state lasers were developed for spectroscopic applications. Wavelength modulation was achieved via amplitude modulation of the pump laser power as well as via piezo driven mirror shakers.

6) Demonstration of organic molecular trace-gas detection in the multi-pass cell with sensitivity 0.11 ppbv using developed tunable mid-IR laser source.

5.2 Future Work: Integration of a Single Frequency Cr\(^{2+}\) doped ZnS Broadband Laser with QEPAS Detector - “Optical Nose” Platform

A compact portable platform (“Optical Nose”) to be developed in future will be used for sensing of organic and inorganic molecules with absorption lines within 1.9-3 \(\mu\)m spectral range covered by the radiation of tunable Cr\(^{2+}\):ZnS lasers described in previous chapter. The absorption lines for selected chemicals in the 1.8–3.2 \(\mu\)m waveband [52] are depicted in Figure 74.
Figure 74. Absorption lines for selected chemicals in the 1.8–3.2 µm waveband taken from the Hitran 2004 database – the numbers on the right correspond to the number of discrete absorption lines.
Recent progress [53] in the area of Photoacoustic Spectroscopy relates to a new approach based on utilization of a quartz tuning fork (QTF) as a resonant acoustic transducer. The main idea is that instead of using a gas-filled resonant acoustic cavity and microphones as in traditional photoacoustic spectroscopy the sound energy can also be detected using a high Q piezoelectric crystal element. Specifically sensitive lock-in amplifier is used to measure QTF piezo-current converted into voltage as a function of pump wavelength. This new QEPAS approach takes advantage of the extremely high quality factor Q of quartz crystals [53]. Moreover, in addition to high sensitivity and convenience this configuration offers simple and compact design of an acousto-optical cell, immunity to an environmental acoustic noise and ability to analyze contents in volume not exceeding 1 mm³ (see Figure 75).

![Quartz tuning fork from electronic clock resonating at 32768 Hz.](image)

**Figure 75.** Quartz tuning fork from electronic clock resonating at 32768 Hz.

The integration of the mid-IR tunable laser with quartz tuning fork platform will consist of the following parts:
(1) Integration of quartz crystal resonator with the Brewster window optical cell. The tuning fork to be used in our work will be a quartz crystal resonator (AEL crystals) with a specified frequency of 32.768 kHz in the oscillator circuit. The optical gas cell enclosing the fork will have a small volume of ~3 cm$^3$. CaF$_2$ windows will be installed at Brewster's angle on either end of the cell. The gas intake will be positioned just above the tuning fork so that gas would flow directly between the prongs and the effective gas sampling volume will be minimized. The gas output will be connected to a membrane pump through a needle vent, to regulate the pump capacity, and a dampening volume, to prevent any pump noise from reaching the tuning fork.

(2) Fiber pumped Cr:ZnS tunable laser source modulated at 16kHz repetition rate will be integrated with QEPAS detector in terms of resonance frequency and spatial alignment.

(3) The experimental set-up (see Figure 76) will be assembled, calibrated, and validated by performing detection of NH$_3$ molecules at sub ppm level of concentration.

Figure 76. “Optical Nose” platform based on QEPAS technique.


21 J. Kernal, V. V. Fedorov, A. Gallian, S. B. Mirov, V. Badikov, “3.9-4.8 μm gain-switched lasing of Fe:ZnSe at room temperature”, Optics Express, 13, 10608-10615 (2005).


51 http://www.pnl.gov/

http://vpl.astro.washington.edu/spectra/c2h6pnlimagesmicrons.htm

