

# Recent progress and applications of mid-IR lasers based on transition metal doped II-VI semiconductors

#### **Sergey Mirov**

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- The work reported here partially involves intellectual property developed at the University of Alabama at Birmingham. This intellectual property has been licensed to the IPG Photonics Corporation. The UAB co-authors declare competing financial interests.

1

UAB Innovative Forum: Middle-infrared Technologies for Environment,

# What do we need solid state mid-IR lasers for?

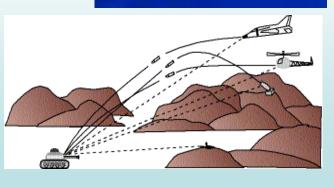
- Sensing
  - Organic molecular fingerprints
  - LIDAR
- Medicine & Dentistry
- Material processing





- Free space communication
- Defense related applications
  - Target designation
  - IR countermeasures

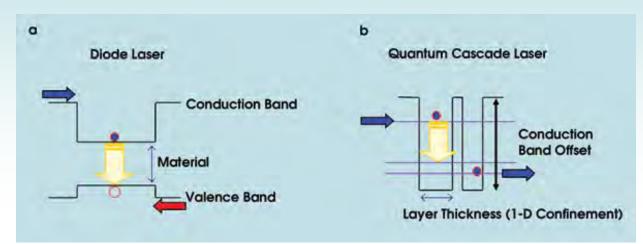


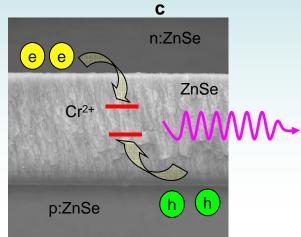






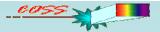
# Three different semiconductor technologies for direct lasing in Mid-IR



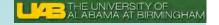


- a) A diode laser generates light from the recombination of electrons and holes across the semiconductor's bandgap, and the material's bandgap determines the wavelength of emission.
- b) In a quantum cascade laser, light is generated from an energy transition in the conduction band of a semiconductor superlattice. By changing the thicknesses of the quantum wells and barriers in the superlattice, we can change the wavelength of light emitted.
- c) In transition metal doped II-VI semiconductors light is generated from an energy transition of Impurity excited optically or electrically.

3



#### **Motivation for transition metal**



## (e.g. Cr<sup>2+</sup>, Fe<sup>2+</sup>) doped II-VI (e.g. ZnSe) semiconductor lasers

For femto-chemistry, molecular time-resolved measurements, molecular spectroscopy, trace gas analysis, biomedical applications, etc. one should directly reach molecular fingerprint 2-20 µm region.

→ Mid-IR tunable, cw-fs sources are required

#### **Requirements:**

- Sufficient bandwidth
- Low cost, compact, directly diode-pumped  $\rightarrow$  low threshold
- High brightness, i.e. good spatial coherence ( $TEM_{00}$ ).

#### **Solutions:**

**Athmospheric** transmission

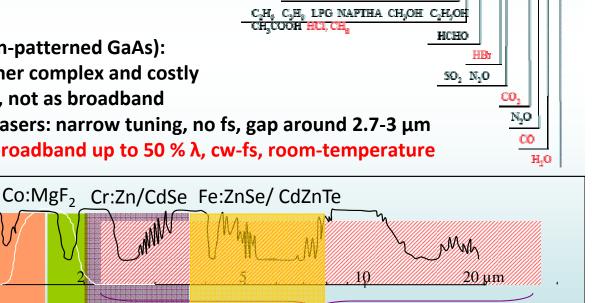
0.2

- OPO (bulk ZGP, PPLN, orientation-patterned GaAs): almost ideal solutions, but rather complex and costly
- QCL: nice solution for  $\lambda > 3.4 \mu m$ , not as broadband

Ti:S/Cr:LiSAF

0.5

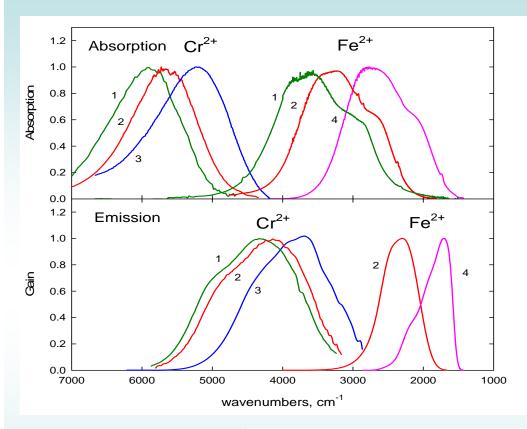
- Semiconductor InGaAsSb/GaSb lasers: narrow tuning, no fs, gap around 2.7-3 µm
- Crystalline vibronic lasers: ultrabroadband up to 50 % λ, cw-fs, room-temperature



CH, C,H, CHCl, C,H,Cl



## Cr2+ and Fe2+ in ZnS, ZnSe, CdSe



➤ High emission and absorption cross section (10<sup>-18</sup>cm<sup>2</sup>)

#### Cr2+

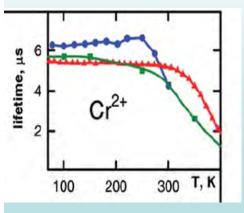
- High luminescence quantum yield
- Broad emission band 1.8-3.7 μm
- Number of available pump sources for Cr<sup>2+</sup>

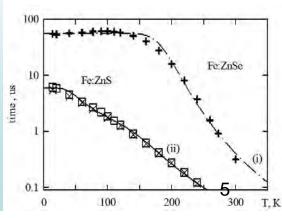
■CW	>22W
Free running	> 1 <i>J</i>
	_

■GS >20mJ

■Peak Power >1GW

■ Mode Locked <50fs, 1W





#### Fe<sup>2+</sup>

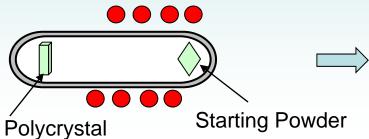
- ➤ Broad emission band 3.0-6.1µm
  - CW >1000 mW
  - Free running>400 mJ
  - GS > 5mJ





## Bulk Crystal Preparation by a quantitative post-growth thermal diffusion

Chemical vapor transport polycrystal growth or IR window purchase



- Post-growth thermal diffusion

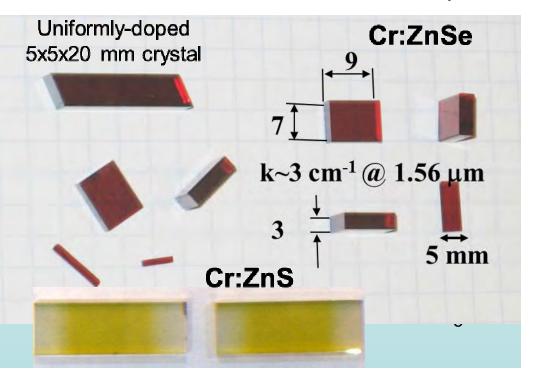
  Dopant

  Polycrystal

  P=10-5 torr

  T- 950-1000 C

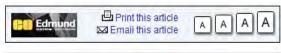
  ut=3-10 days
- Fast diffusion of dopant with suppressed sublimation in Zn and Se sub-latticies.
- Low scattering loss (1-2 % per cm) in thermally diffusion doped crystals;
- Uniformly-doped, reasonably large samples up to 7 mm thickness;
- Quantitative technology enabling pre-assigned concentration of dopant with accuracy better than 3%
- Good for High-Power (tunable) Lasers



## **UAB Mid-IR Laser Materials and Lasers are featured** in the Laser Focus World and Photonics Spectra



Home > Current Issue > Laser Focus World > Article Display



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#### PHOTONIC FRONTIERS: MATERIALS FOR SOLID-STATE LASERS: New materials expand capabilities of solid-state lasers



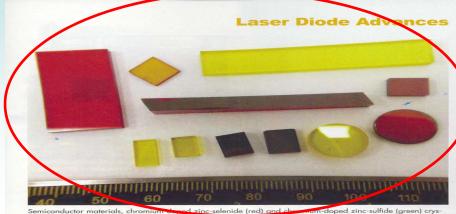
Ceramic hosts, transition-metal doping of II-VI hosts, and optically pumped semiconductor lasers are expanding the range of solid-state laser capabilities to new wavelengths and higher powers.



## Jeff Hecht contributing editor

Although pump sources and cavity designs have evolved over the years, the raw materials for solid-state lasers have been slow to change. Solid-state physics is a complex field, and it has long been cheaper and easier to refine established laser materials such as glass, YAG, and YLF, than to develop new materials for commercial use.

That situation is changing, however, as decades of basic research are producing a better understanding of laser materials. New solld-state lasers are crossing the threshold of practicality, including semiconductors that are optically pumped rather than powered electrically. Three of the hottest new classes of materials are challenging the old standards: ceramic laser hosts, II-VI crystals such as zinc selenide doped with transition metals, and optically pumped semiconductor lasers (OPSLs).



Semiconductor materials, chromium de cid zinc-selenide (red) and element-doped zinc-sulfide (green) crystals, could be used for mid-infrared lasers and, perhaps, eventually in laser diodes. These crystals were fabricated at Photonics to these crystals were fabri-

mid-IP diode lasers that are troadly tunable.

Airov noted that a tuning capability could be very useful. Water absorbs strongly at 2.7 µm and much less so at other wavelengths in the tunable range. This absorption enables a more than the sandfold dynamic range of penetration of this laser light in soft tissue, leading to apotential application.

"As a laser scalpel, it can be a beautifu commercial system," he said.

Cutting and welding plastics are other potential uses of chromium-doped zinc-selenide lasers. Again, the key is the ability to tune the emission so that it hits an absorption peak of the material being processed.

Mirov is doing his part to make such possibilities a reality. Besides conducting research into lasting materials such as zinc selenide and zinc sulfide, he is president of the Birmingham-based Photonics Innovations Inc., a company he helped found to commercialize the technology.

He noted that chromium-doped zincselenide crystals are a mid-IR analog of Ti:sapphire, the workhorse laser material in the near-IR. One problem that has held zinc selenide back has been the difficulty in growing high-quality crystals from t. But, he said, his group has overcome that issue.

e word is plastics

Ainally, there is the possibility of a whole new class of laser diodes as researches work to create lasers using con-

ducting plastics. One benefit could be emission wavelengths virtually anywhere in the visible spectrum, thanks to the ability to tune the electrical and optical properties of polymers across a wide range.

Dr. Paul N. Stavrinou, a physicist from Imperial College London, noted that some recent advances are bringing the creation of such a device closer to reality. For example, the group he is working with reported on the achievement of high conductivity and high gain from the same polymer in a Nature Materials paper last year. In the past, he noted, it was either one or the other. Importantly, both seem desirable for a good laser structure.

Other researchers have demonstrated a degree of integration of injection layers and optical gratings into an overall structure. The development of these device architectures is important because a successful polymer laser will have to combine conductive layers, a grating and a gain material in a manner compatible with organic and polymer chemistry.

Stavrinou said another hurdle will be in understanding how to achieve continuous-or quasi-continuous-wave operation. He hopes that these problems will be solved, helping to make plastic laser diodes feasi-

Such a reality could be closer than it looks because key developments are at hand, Stavrinou said. "I do think it very likely an electrical injected polymer laser will be demonstrated soon. The elements required are all actively being realized."

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Photonics Spectra August 2009

# That's One Bright Idea.

## UAB Mid-IR Laser Materials and Lasers are featured in the J. International Innovation, September 2012

DR SERGEY MIROV

#### Tuning in

Researchers at the **University of Alabama at Birmingham** have been producing infrared laser technology with unprecedented tunability, and now their work is nearing commercial availability

MID-INFRARED (mid-IR) LASERS have a large number of important applications, providing their wavelength is sufficiently flexible for sensing purposes. The lasers are able to offer medical, environmental, scientific and counterterrorism applications, including the detection of explosives, chemical and biological warfare agents and their precursors. They are also useful in industrial process control, and the measurement of medically important molecular compounds in the exhaled breath of patients. The new technology, which uses transition metal (TM) impurities embedded within semiconductors, moves beyond the capabilities of currently available products. Against semiconductor lasers, or quantum cascade laser technology, the new laser structure is set to provide a far greater flexibility in usage. There are significant improvements in bandwidth, as well as broader tunability, excellent for sensing applications, and also ultra-short pulse generation. There is also the possibility significantly higher output energy than available in semiconductor lasers. In comparison with solid state lasers, the obvious advantage of electrically pumped lasers based on TM doped II-VI structures is in more convenient direct electrical excitation.

The team at the University of Alabama at Birmingham is investigating the possible approaches for advancing this form of lasers, hoping to press forward with this technology based on iron, cobalt and chromium dopants.

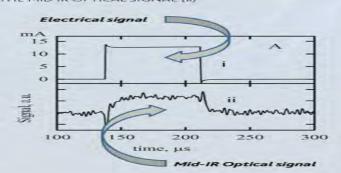
Attempting to produce a laser which can provide an extended range of wavelengths and powers has been an extremely challenging task, however the group has been able to make a number of significant breakthroughs in their work. They have already developed an efficient technology for post-growth doping of a number of crystals, providing a low-loss, uniformly doped gain material, as well as an option for hot pressing of TM doped II-VI powders directly into the laser ceramic. They have pioneered the first sulphide and chromium-zinc selenide microchips, and have also demonstrated a gain switched room temperature iron-zinc selenide mid-IR laser. The lasers with chromium ions have achieved over a 20W output at a real efficiency of over 50 per cent. There have been a large number of other innovations, but a major part of the team's success has been the adoption of their technology by a commercial supplier. TM doped II-VI gain media, and multiple mid-IR tunable lasers have now become commercially

available from a partner organisation, IPG Photonics Corporation. The technology is now set to go from strength to strength, with the team's innovative research working alongside the commercial production of lasers, research and commercial interests operating in synergy.

#### APPROACHING INNOVATION

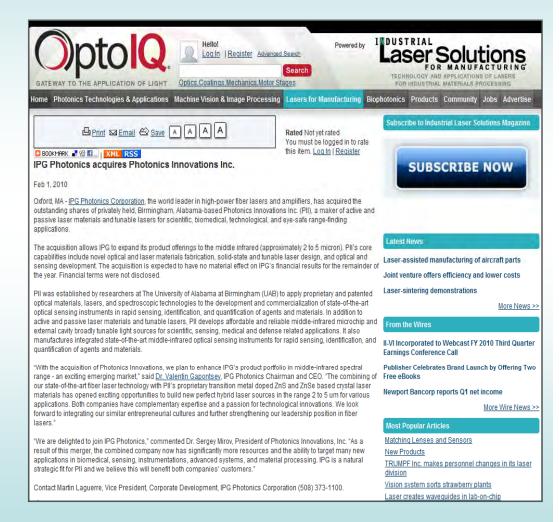
The development of products is testament to the researcher's hard work, yet they did not set out to produce commercially available lasers. Dr Sergey Mirov, who is leading the study, instigated the project: "Initially, we worked for pure scientific interest, studying new and interesting aspects of solid state physics, but in the course of research it became clear for us that transition metal doped II-VI lasers combine the versatility of the ion-doped solidstate lasers with the engineering capabilities of semiconductor lasers". As they continued their work, the researchers were able to see that their approach was leading towards the production of electrically pumped lasers with unprecedented bandwidth in the mid-IR part of the spectrum. At this point, the drive for the potential applications of such a system of lasers, or commercialisation meant that the research built momentum, working towards the position which the team is now in. Aiming for the numerous potential applications in the

FIGURE 1. OSCILLOSCOPE TRACES OF THE ELECTRICAL CURRENT ACROSS THE ALCR. ZINSE SAMPLE (I) AND THE MID IN OPTICAL SIGNAL (II)

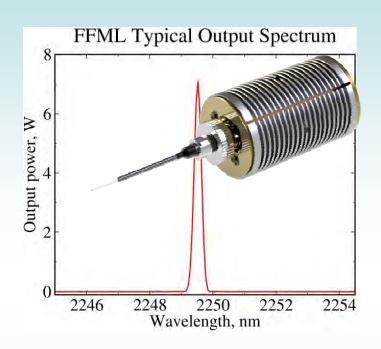


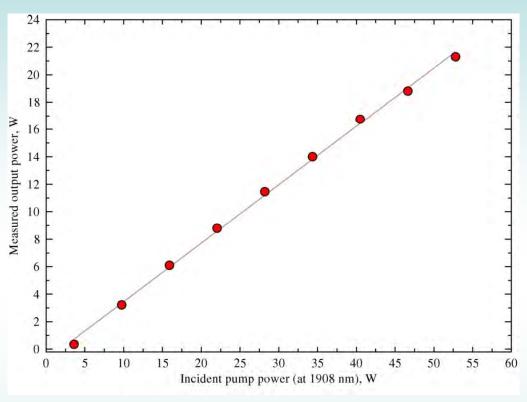
### **Commercialization**

- "One local startup is Photonics Innovations is founded by OS researchers and produces middleinfrared gain materials and lasers out of Innovation Depot."
- □ UAB-OS start-up Photonics Innovations, Inc. was acquired by IPG Photonics Corporation, world leader in fiber laser technology.
- UABRF has negotiated the terms and signed license agreement with IPG Photonics Corporation to enable the company to utilize mid-IR platform technologies as well as to develop commercial applications.



## High Power Cr:ZnSe/S fiber-bulk mid-IR hybrids





#### Model FFML-Cr-ZnSe/S-2.25-5

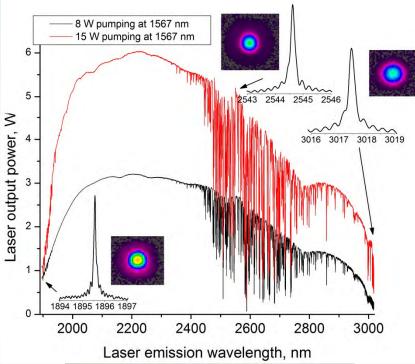
- ■Multi-Watt Output Power
- Narrow-line fixed wavelength
- ■Wavelengths within 2000 3000 nm available

#### **Target Applications**

- ✓ Plastic Processing:
- Cutting & Welding
- Marking & Drilling
- ✓ Medical Applications:
- Tissue & Bone Cutting
- Dental Applications
- Skin Rejuvenation



### Cr:ZnSe/S Narrow Line Tunable Laser





#### ☐ Model HPTLM-CrZnS/Se-2400-3000

- ☐ Multi-Watt (20W) Output Power
- Narrow Linewidth Operation, <0.1 nm available</p>
- ☐ Tunable wavelength range up to 1200 nm (with one set of optics)
- Any central wavelength within 2-3μm
- □ TEM<sub>00</sub> Output Beam Quality

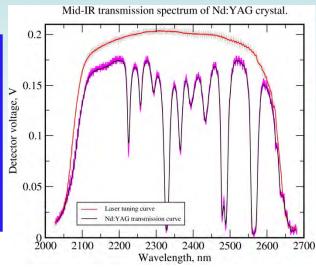
#### **□** Applications

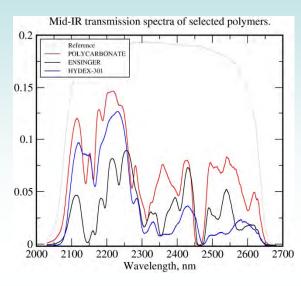
- □ Spectroscopy
- □ OPO Pump Source
- Medical Applications
- Environmental Monitoring
- Industrial Process Control



# Rapidly Tunable Laser Module RTLM-Cr-ZnS-Se-2350-1000







Sample spectroscopic measurements. The acquisition time for each spectrum

#### MAIN FEATURES

- Up to 1000 spectra per second (i.e. 1kHz wavelength tuning rep rate).
- Milli-Watt to Multi-Watt Output Power
- Narrow Linewidth Operation, 0.05-0.5 nm available\*
- Tunable wavelength range up to 700 nm
- $\bullet\,$  Any central wavelength within 2-3  $\mu m$
- TEM<sub>00</sub> Output Beam Quality

\* Single-Frequency rapidly-tunable module is under development

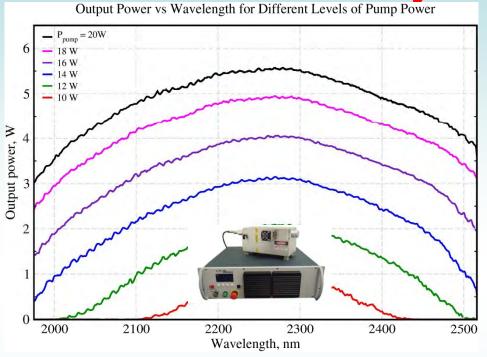
#### **APPLICATIONS**

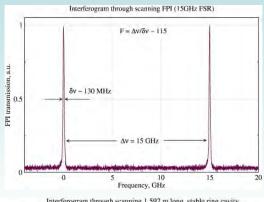
- Rapid Laser Spectroscopy
- Medical Applications
- Environmental Monitoring
- Industrial Process Control
- Material processing

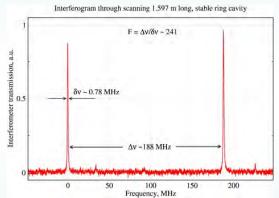


Cr:ZnSe/S single-frequency tunable fiber-bulk

hybrids







#### Model SFTL-Cr-ZnSe/S-2200-5000

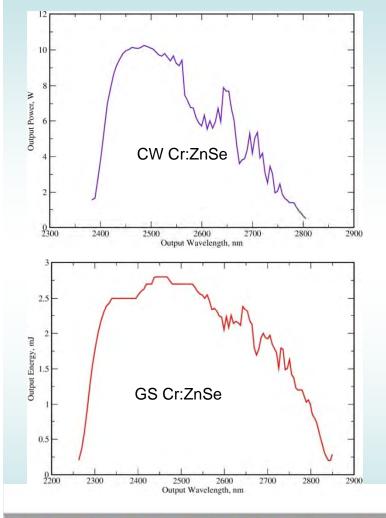
- Multi-Watt Output Power
- Narrow Linewidth, <1 MHz</li>
- Large tuning range with a single set of optics (any wavelength within 2000 -3000 nm tuning range is available)

#### **Target Applications**

- High Resolution Spectroscopy
- OPO Pump Source
- Medical Applications
- Environmental Monitoring
- Industrial Process Control
- Material processing
- Free Space Communications



# 2 Channel Integrated CW high power tunable and gain-switched high energy tunable Cr:ZnSe laser



#### **Main Features**

- ☐ Tunability 2300-3000 nm
- ☐ CW Channel Output power 10
- ☐ GS Channel Output Energy up to 3 mJ
- ☐ Pulse Duration 5-20 ns
- ☐ Repetition Rate 0.1-1 kHz
- ☐ TEMoo Output Beam Quality

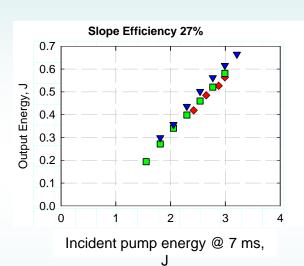


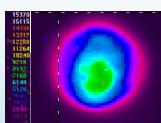


## High Energy Free Running Cr:ZnSe mid-IR laser

#### **Pump source**

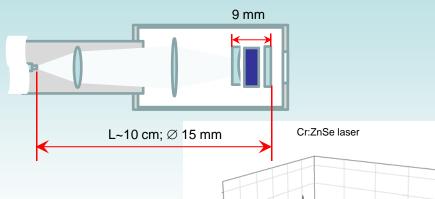
Palomar Er –glass laser

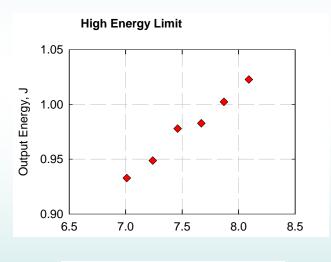


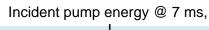


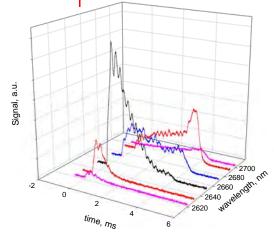
#### **Pump Laser Specs**

- 1.  $\lambda = 1540$  nm.
- 2.  $E_{max} = 10J$
- 3. D=800 um.
- 4. NA=0.15







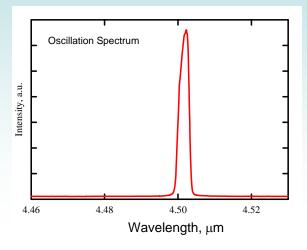


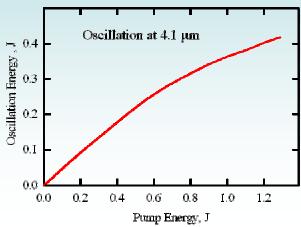
#### Cr:ZnSe Laser

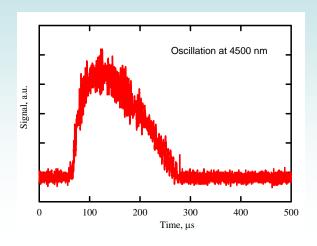
- 1.  $\lambda = 2650 \text{ nm}$ .
- 2.  $E_{\text{max}} = 1.05 \text{ J}$ 
  - 3.  $\tau$ =5-7 ms

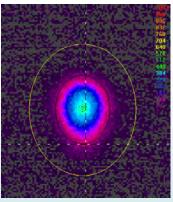


## High Energy Free-Running, Pulsed, Fixed Frequency Fe:ZnSe Laser: Model PFFL-Fe-ZnSe









#### MAIN FEATURES

- Any wavelength within 3.9-5.1µm available
- High Output Energy >400 mJ
- Pulse Duration 200 μs
- Max. Repetition Rate >30 Hz

#### **APPLICATIONS**

- Spectroscopic
- Sensing
- Medical
- Defense related applications
- Seeding, or pumping middle-infrared optical parametric oscillators



# CW Narrowline Mid-IR Tunable Fe:ZnSe Laser

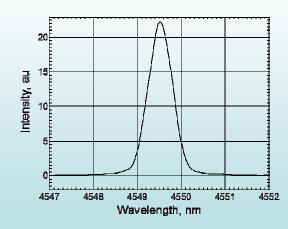
#### MAIN FEATURES

- Any wavelength within 3.7-4.8µm available
- Output Power >300 mW

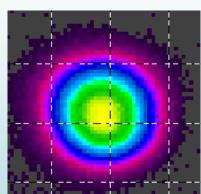
#### **APPLICATIONS**

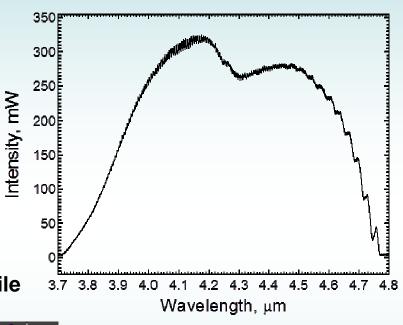
- Spectroscopic
- Sensing
- Medical
- Defense related applications
- Seeding, or pumping middle-infrared optical parametric oscillators

#### Laser linewidth



#### **Output beam profile**





**Typical Tuning Curve** 

## Gain Switched Mid-IR Fixed Frequency or Tunable Fe:ZnS/Se Lasers

#### Main Features:

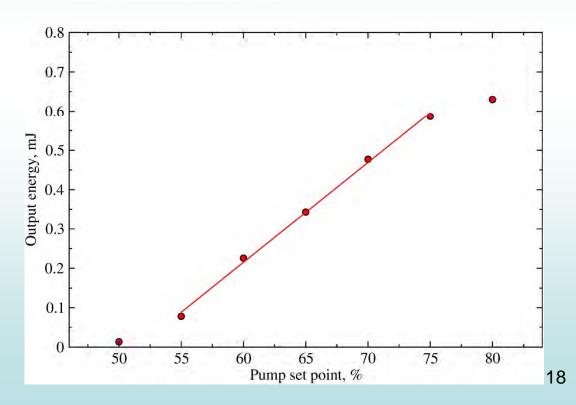
- Output wavelength within 3.6-5.0µm
- Output Energy >0.5 mJ
- Pulse Duration 2-20 ns
- Repetition rate 0.1-1 kHz
- TEM<sub>00</sub> Output Beam Quality
- Room Temperature Operation

#### Typical Applications:

Medical Applications
Environmental Monitoring
Industrial Process Control
Materials Processing
Sensing
MALDI Mass Spectroscopy



Typical output-input characteristics of Fe:ZnS laser operating at 3950 nm at 1 kHz rep. rate at RT



## Middle-Infrared Pulsed/CW Material **Processing Station**

#### LASER OPTIONS

- Pulsed: 2.1-2.7 um, 5-20\* mJ, variable pulse rate (0.1-1kHz)
- CW: 2.0-3.0 um, 5-20\* W
- Dual-Wavelength (switchable)
- Continuously tunable option
- Gaussian/Flat-Top beam profile options





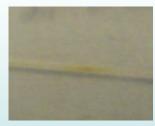
Weld of transparent textured polymer film (0.4 mm thick)



Weld of transparent PET



film (0.1 mm thick)



Weld of transparent ETFE film (0.2 mm thick)

#### MAIN FEATURES

- · Class I laser safety enclosure
- Precision XYZ positioning stage
- · Galvanometer beam steering
- CNC Controller
- Scan lens for small feature processing
- Variable beam spot at target plane option
- · Vacuum chuck options
- · Visible guide beam
- · Coaxial high-resolution camera

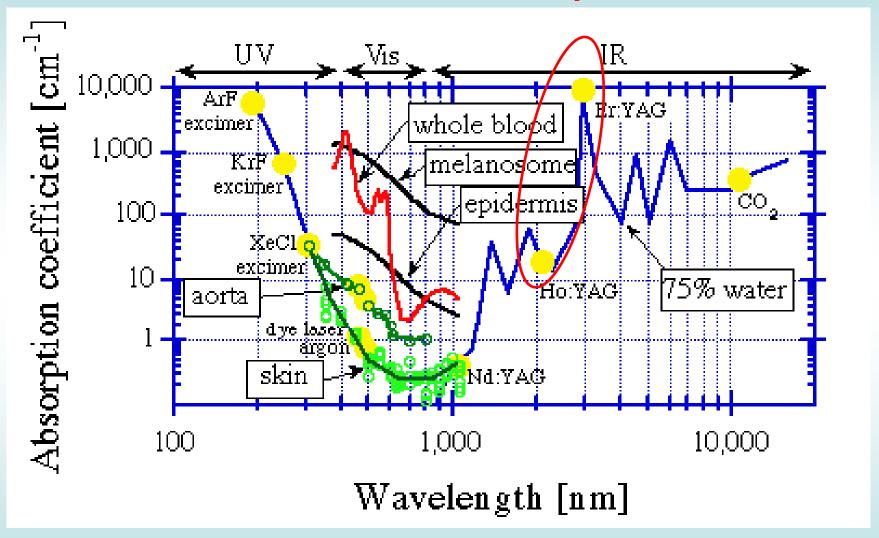
#### **APPLICATIONS**

- Polymer material processing (Welding, Cutting, Drilling, Marking, Ablation)
- · Medical research applications
- · Medical materials processing

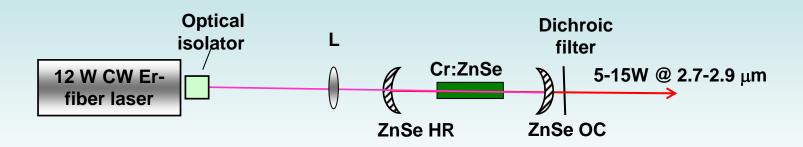
#### Advantages of Mid-IR lasers for polymer processing:

- Strong, broad absorption lines in 2-3um spectral range
- Variable penetration depth
- No contrast additives required

### **Future Mid-IR Laser Scalpel**



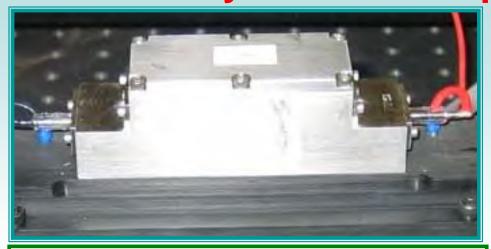
### Medical application of UAB mid-IR lasers. Skin resurfacing



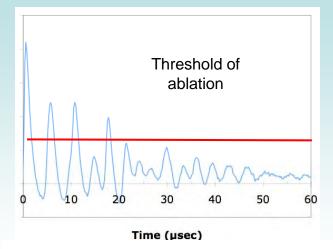


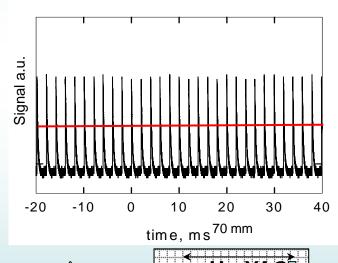
Skin resurfacing procedures; the photocoagulation of pigmented lesions, such as lentigos (age spots), solar lentigos (sun spots) and dyschromia; melasma; treatment of periorbital wrinkles and for dermatological conditions requiring the coagulation of soft tissue.

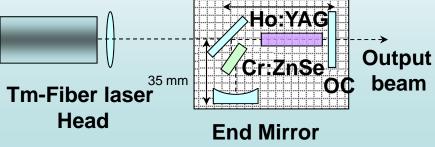
## Fiber-bulk hybrids – new approach for dental lasers







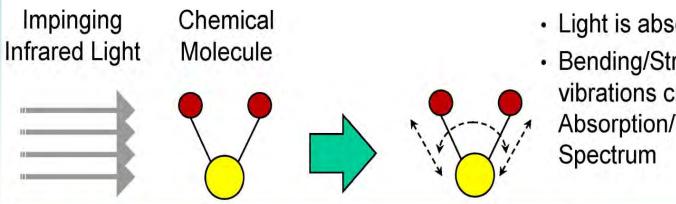








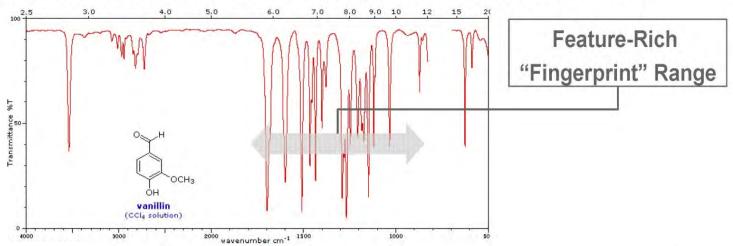
## What is mid-IR absorption spectroscopy- "optical nose"?



- · Light is absorbed
- Bending/Stretching molecular vibrations create "fingerprint" Absorption/Transmission

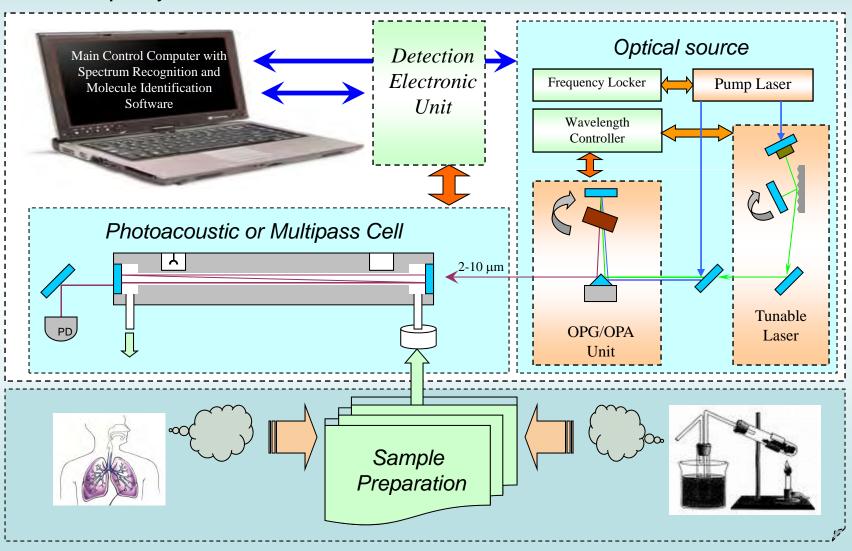
The 2-15 µm spectral region is the most desired region by spectroscopists

#### Resultant Transmission Spectrum – Mid-Infrared Radiation (2-20 μm)



### **Middle-infrared Optical Nose**

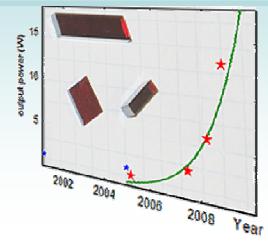
- □By rapidly tuning the wavelength of the OPG, the absorption of a gas mixture is measured as a function of the wavelength.
- □The instrument will be capable of identifying a large variety of molecular organic trace-gases in multi-compound gas-mixtures and to quantify them at ultra-low concentration levels in real time.

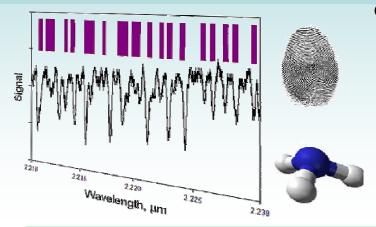






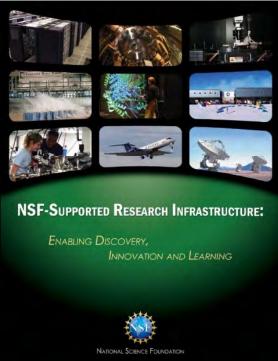
### "Optical Nose" system





Optical detection of the trace ammonia and ethane using "Optical Nose" detection system

The system sensitivity was equal to 5 ppbv for ethane and 0.11 ppbv for ammonia



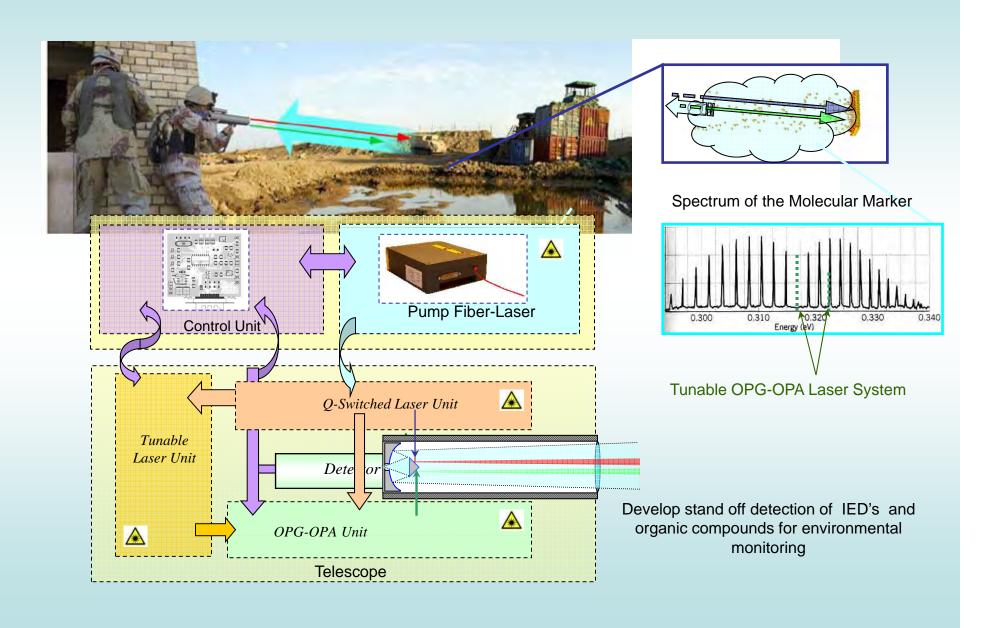
## Researchers Develop Mid-infrared Laser "Optical Nose"

Researchers at the University of Alabama at Birmingham, supported by an MRI grant, have developed a powerful system combining three types of lasers that could rapidly detect a wide range of substances in complex mixtures, including trace gases at the parts-per-trillion level. Designed to detect and identify many types of organic molecules, the system combines high power, low noise and coverage of the infrared spectrum that matches a large library of molecular energies. Potential uses for the "optical nose" include detecting the presence of oil, pollutants in the atmosphere, harmful chemical or biological substances, or the early stages of disease. For more information, see the NSF award abstract at http://www.nsf.gov/awardsearch/showAward. do?AwardNumber=0521036c

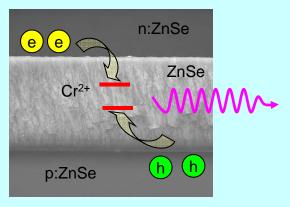


A team of researchers at the University of Alabama at Birmingham, led by physics professor Sergey Mirov, developed a novel laser-based "optical nose" for the capid identification and quantification of organic trace-gases in multi-compound gas mixtures with full biochemical specificity and high sensitivity. Above, Omitri Martyshkin uses the optical nose for sensing hydrogen flooride molecules. Credit: Courtesy Sergey-Mirov, University of Alabama at Birmingham

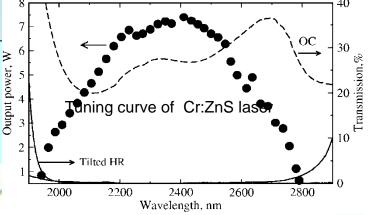
# Future activities (Stand-off detection of the organic compounds )

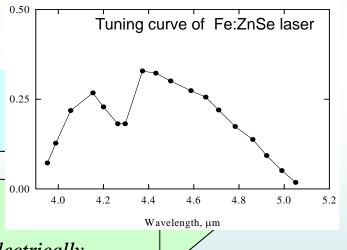


## Future Electrically pumped MID-IR LASER based on TM doped II-VI semiconductors



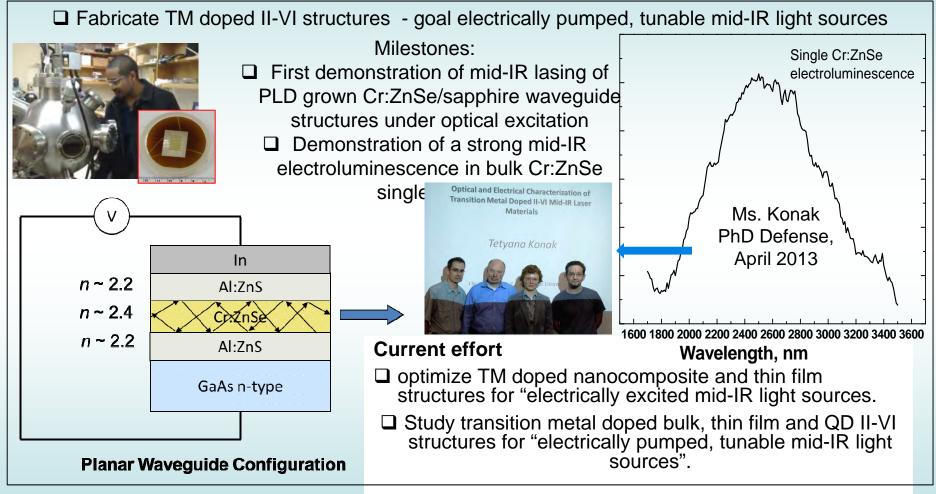
We are going to use developed techniques to fabricate thin films and quantum dots of ZnSe and ZnS doped with Chromium samples for enhancement of the electrical excitation of the transition metals.





p-n junction structures for compact, electrically pumped broadly tunable mid-IR laser sources based on TM ions in II-VI Materials

# Development of electrically pumped mid-IR lasers for ultra-portable trace gas detection systems



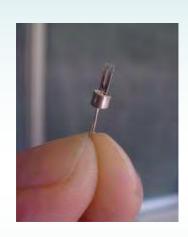
- J. E. Williams, V.V. Fedorov, D. V. Martyshkin, R. P. Camata, and S. B. Mirov; "Mid-IR laser oscillation in Cr<sup>2+</sup>:ZnSe planar waveguide," *Optics Express* **18**, 25999-26006 (2010).
- S.B. Mirov, V.V. Fedorov, D.V. Martyshkin, I.S. Moskalev, M.S. Mirov, and V.P. Gapontsev, "Progress in Mid-IR Cr2+ and Fe2+ doped II-VI materials and Lasers (invited)", Optical Materials Express, 1, 898-910 (2011).



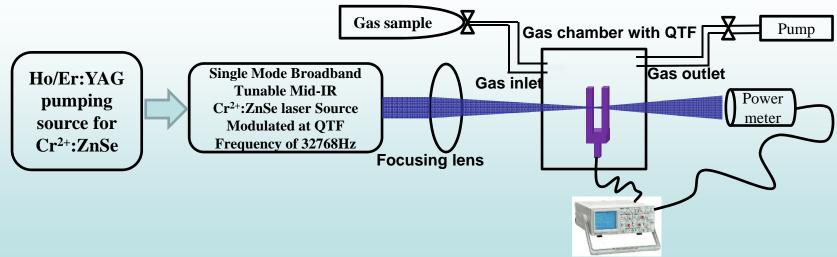


## Future Quartz Enhanced Photo-Acoustic Spectroscopy "QEPAS- Optical Nose"

QEPAS allows to increase sensitivity of few orders of magnitude with respect to PAS



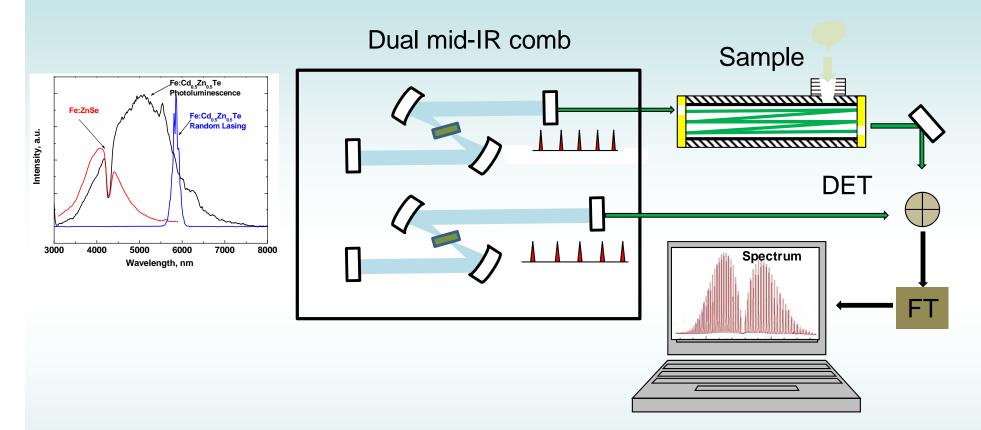
 $f_0 = 32 768Hz = 2^{15} Hz$ High stability Compactness Sample size ~ 1mm<sup>3</sup>







## Future Dual Frequency Comb Optical Nose



Two similar mid-IR femtosecond oscillators have slightly different line spacing. One of the beams interrogates a multiple-pass cell, which contains the analyte and than both radiations are heterodyned against each other on a single fast photodetector, yielding a down-converted radio-frequency comb containing information on the absorption losses experienced by each line of the interrogating fs laser. The electrical signal is digitized and is Fourier transformed using a fast Fourier-transform algorithm.

# Mid-IR Lasers Closing words. Analogy with Ti:sapphire

- The Ti:sapphire laser was the result of about a decade of concentration on a single idea - tunable near-IR solid state lasers.
- Thank you (not) MIT Patent Office (the old one)
- Estimate that over \$600
  million in laser systems
  have resulted, along with
  at least two Nobel prizes



- The Cr:ZnSe/S laser was also the result of about a decade of concentration on a single idea - tunable mid-IR solid state lasers.
  - Thank you UAB RF
  - Hope to show at least the same performance

# **Acknowledgements COSS Associates**

