Twin $HgGa_2S_4$ optical parametric oscillator at 4.3-10.78 μm for biomedical applications

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ABSTRACT

We demonstrate an optical parametric oscillator (OPO) based on two $HgGa_2S_4$ (HGS) crystals with exceedingly wide tuning range from 4.2 μm to 10.73 μm. The HGS OPO was pumped by Q-switched Nd:YLF laser at 1.053 μm with a 5-7 ns pulse duration. Absorption spectrum of ammonia was presented to demonstrate the feasibility of the OPO system for spectroscopic measurements and gas detection.

Keywords: optical parametric oscillator, photo-acoustic spectroscopy, molecular biomarkers, ammonia

1. INTRODUCTION

Widely tunable mid-infrared laser sources are of great interest for various scientific applications such as trace gas or biomedical sample detection, remote sensing, environment monitoring and other. Using of widely tunable mid-infrared laser sources allow to separate contribution into the common spectra of various molecular components of biological tissues and biological liquids, to control dynamics of metabolic processes.[1] One of the most important processes in the human body is endogenous and exogenous gas exchange with the environment, basing on the excretion of metabolic products.

Exhaled air contains up to 3000 volatile compounds, including molecule biomarkers, which have specificity sufficient to study both normal and pathological processes. As a example, principal component analysis of absorption spectra of sputum of 25 patients with lung cancer and 25 healthy volunteers in the 1800-950 cm^{-1} range allowed to identify the whole group of lung cancer patients and 92% of healthy volunteers.[2] The most informative areas of the spectrum are: 964 cm^{-1}, 1024 cm^{-1}, 1411 cm^{-1}, 1577 cm^{-1} and 1656 cm^{-1}.

The concentrations of some substances contained in the exhaled air of healthy people, are presented in table 1. One of them is ammonia which formed during the hydrolysis of the urea when urea is decomposed into ammonia and CO_2, both components diffuse into the blood and then excrete through the lungs. The content of ammonia in the breath is also associated with increased respiratory symptoms and asthma.[3] The level of exhaled ammonia significantly increased during infections of the respiratory tract, and the control of its content can differentiate viral and bacterial infections in several lung diseases.[4]

Ammonia has reach absorption spectrum in a region of 9-10 μm (Fig. 1) which can be measured using CO_2 laser gas analyzers. There are hardware implementations of the method of photo-acoustic spectroscopy with a tuning range of 5-18 μm on the basis of free electron laser[5], however, such equipment has significant mass-dimensional parameters and is applicable only for laboratory research.

Optical parametric oscillation is one of the most widespread ways to generate tunable coherent radiation in the spectral range from visible to mid-IR. Most often nonlinear crystals used in mid-IR OPO are silver thiogallate $AgGaS_2$ (AGS) and mercury thiogallate $HgGa_2S_4$ (HGS). The main feature of both crystals is that HGS and AGS can be pumped near 1 μm by commercially available laser (e.g. Nd:YAG, Nd:YLF) without two-photon absorption due to its wide band-gap (2.73 for AGS and 2.79 for HGS).[6]

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Table 1. Concentration of certain substances in exhaled air.[7]

Metabolic product	Average concentration
CH_4	2-10 ppm
C_2H_6	0-10 ppb
C_5H_{12}	0-10 ppb
NO	10-50 ppb
CO	1-10 ppm
CSO	0-10 ppb
N_2O	1-20 ppb
C_5H_8	50-200 ppb
NH_3	0-1 ppm
C_3H_6O	0-1 ppm

In spite of the fact that AGS the standard non-oxide mid-IR material HGS is more attractive nonlinear optical material for OPO due to its high nonlinearity, high damage threshold and good heat conduction.[8] HGS has a transmission range extending from 0.55 μm to 11 μm.[5] Comparing HGS to AGS it relatively high surface damage threshold (315 MW/cm^2, 14 ns)[9] against 30 MW/cm^2 (10 ns) for AGS[6] and relatively high nonlinear coefficient d_{36} = 31.5 pm/V against d_{36} = 17.5 pm/V for AGS[10]. HGS was introduced for nonlinear optical applications as early as 1976.[11] However, using this material for OPO was restricted due to poor optical quality of grown samples. Suitable size HGS samples with good optical quality were grown by Bridgeman-Stockbarger technique in High Technologies Laboratory, Kuban State University in 2003.[12]

Subsequently nanosecond OPO based on HGS was first demonstrated in 2003.[10] The idler tuning range of HGS OPO described in Ref. 12 was 2.3 - 4.4 μm. Later same authors presented HGS OPO with tuning range 3.7 - 5.7 μm.[13] The tuning range was restricted due to crystal dimensions and OPO cavity configuration. Maximum idler energy was 3.3 mJ at 4 μm (67 mW, 20 Hz). The nanosecond OPO based on HGS which was described in Ref. 14 had high idler energy 6.1 mJ at 4.03 μm (610 mW, 100 Hz).This OPO was pumped by Q-switched Nd:YAG laser/amplifier system delivering up to 250 mJ per pulse at 100 Hz with pulse duration 8 ns.

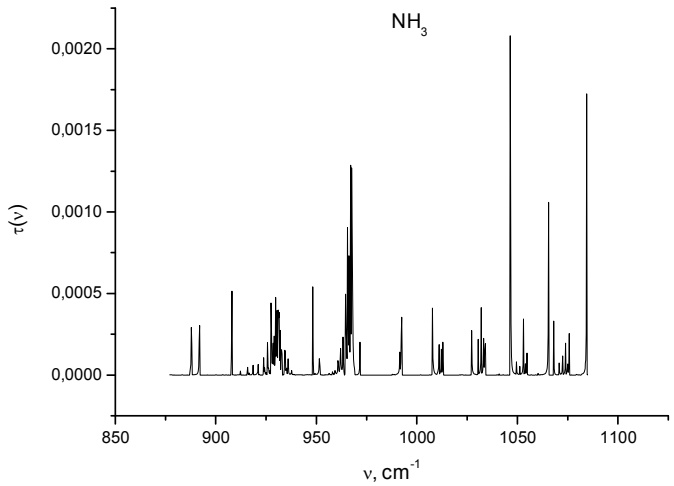

Figure 1. Calculated using Hitran database high-resolution absorption spectrum of ammonia in a region of 9-10 μm.

In the present work we demonstrate nanosecond OPO based on HGS with exceedingly wide tuning range from 4.2 μm to 10.73 μm. We propose a new conception of widely tunable nanosecond optical parametric oscillator based on two HGS crystals switched into the same cavity. Each crystal operate in the own spectral range, but the switching HGS crystal shifts wavelength tuning range to other spectral range. Developed OPO combined with resonant photo-acoustic detector allow creating laser gas analyzer for detection different gases in wide spectral range.

2. EXPERIMENTAL SET-UP

The HGS samples used in the present study were grown by Bridgeman-Stockbarger technique. Samples were cut for type-II (eoe) phase-matching. One sample (sample A) was cut at θ = 60°and φ= 0° for idler wavelength ~ 4.8 μm at normal incidence. The second sample (sample B) was cut at θ = 47°and φ= 0° for idler wavelength ~ 7.5 μm at normal incidence. Both samples were 13 mm-long with an aperture 5 mm × 5mm. These elements are polished and antireflection coated at the same technological block. Surfaces of crystals were antireflection (AR) coated using dielectric layers so that the transmission at 1.053 μm was ~99 %.

The experimental set-up of developed OPO based on two HGS crystals is shown in Fig.2. The experimental set-up consists of the following elements: pumping Nd:YLF laser, Faraday isolator FI, half-wave plate λ/2, mirrors M_1-M_6, pyroelectric detector PD, wavelength meter WM, photo-acoustic detector PAD motorized translation stage MTS, motorized rotation stage MRS, computer PC.

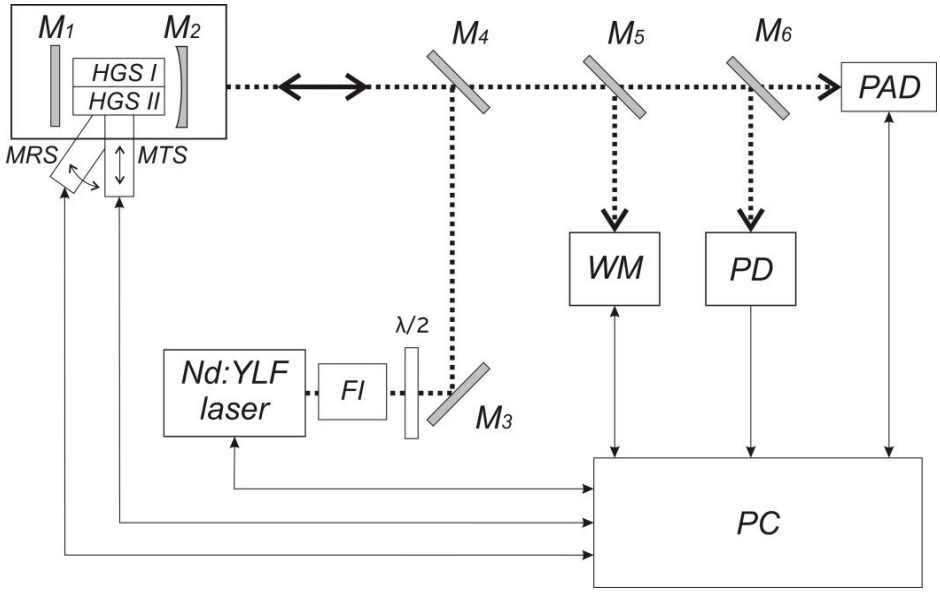

Figure 2. Experimental setup: Nd:YLF laser – pump laser, FI – Faraday isolator; λ/2 – half-wave plate; M1-M6 – mirrors; MTS – motorized translation stage; MRS – motorized rotation stage; WM – wavelength meter; PD – pyroelectric photodetector; PAD – photo-acoustic detector; PC – computer

The pump source is a diode-pumped Q-switched Nd:YLF laser (TECH-1053-N, Laser-compact Group, Russia). The pump wavelength is 1.053 μm, and the pulse duration is 5–10 ns. The maximum laser pulse energy at repetition rate of 100 – 5000 Hz is about 1300 μJ. Pump pulses that passed through the FI and half-wave plate were reflected by mirrors M3 and into the OPO cavity, which was formed by mirrors M1, and M2.

The OPO cavity with a length of 23 mm is formed by the semitransparent M2 (Layertec) and reflecting M1 (Thorlabs) mirrors. The output coupler M2 was transparent for pump and idler and has R=90% for signal. The signal was not totally reflected by the output coupler to avoid extreme intracavity fluence that could damage the crystals. HGS crystals were placed on the OPO cavity inside a thermostat. A Peltier element was used to maintain the optimal temperature of both crystals at a level of 20 - 30°C with an accuracy of 0.1°C. The OPO wavelength tuning was performed via precision rotation of the HGS crystals relative to the optical cavity axis using the MRS and switching between crystals by MTS.

Signal and idler were extracted from the OPO cavity through output coupler M2. Subsequently, idler wave passed through the dichroic mirrors M4, M5, and splitting mirror M6, and then arrived at the PAD, which was described in Ref. 14. The latter was used to record the absorption spectra of various gas mixtures. Signal was reflected by the dichroic mirror M5 to the wavelength meter WM (Angstrom LSAL IR, Russia). The signal wavelength was measured by the WM, and then the idler wavelength was determined by recalculation. Mirror M5 was transparent for the idler. The splitter M6 reflected a part of the idler beam to the pyroelectric detector PD (MG-30, Russia), which was used to measure the OPO power and normalize the PAD data. Electrical signals from the WM, PD, and PAD were sent to the PC for processing and displaying. The pulse repetition rate, pulse energy of pump laser, temperature of crystals, movement of MTS (for switching between two crystals) and MRS were controlled by the PC.

3. HGS OPO: EXPERIMENTAL RESULTS

The obtained idler wavelength tunability was 4.2 - 5.71 μm for the first crystal and 5.7 - 10.73 μm for the second crystal. The total scan time in a spectral range 4.2 - 10.73 μm was less than 2 min.

The OPO pulse energy was measured using an Ophir Vega PE-10C power/energy meter (Israel) placed in front of the mirror M6. The measured idler energy was 4 – 10 μJ in the spectral range 4.2 - 5.71 μm (sample A), the measured idler energy was 1 – 8 μJ in the spectral range 5.7 - 8.5 μm (sample B) and less than 1 μJ at 8 - 10.73 μm.

The experiments were carried out under the following conditions: pump energy was 900 μJ; the pulse repetition rate was 1000 Hz; and the temperature of the HGS crystals was 25°C. The average OPO radiation power was ~10 mW (1000 Hz) at 4.5 μm. The OPO energy monotonically decreased with increasing the wavelength in a spectral range of 8 - 10.73 μm. The OPO threshold was 11 mJ/cm^2. This value agrees with 8 mJ/cm^2 given in Ref. 13.The energy dependence is not symmetric, with stronger decrease at longer wavelengths (Fig. 3) due to an increase of absorption level in mercury thiogallate at wavelengths more than 9 μm.[15]

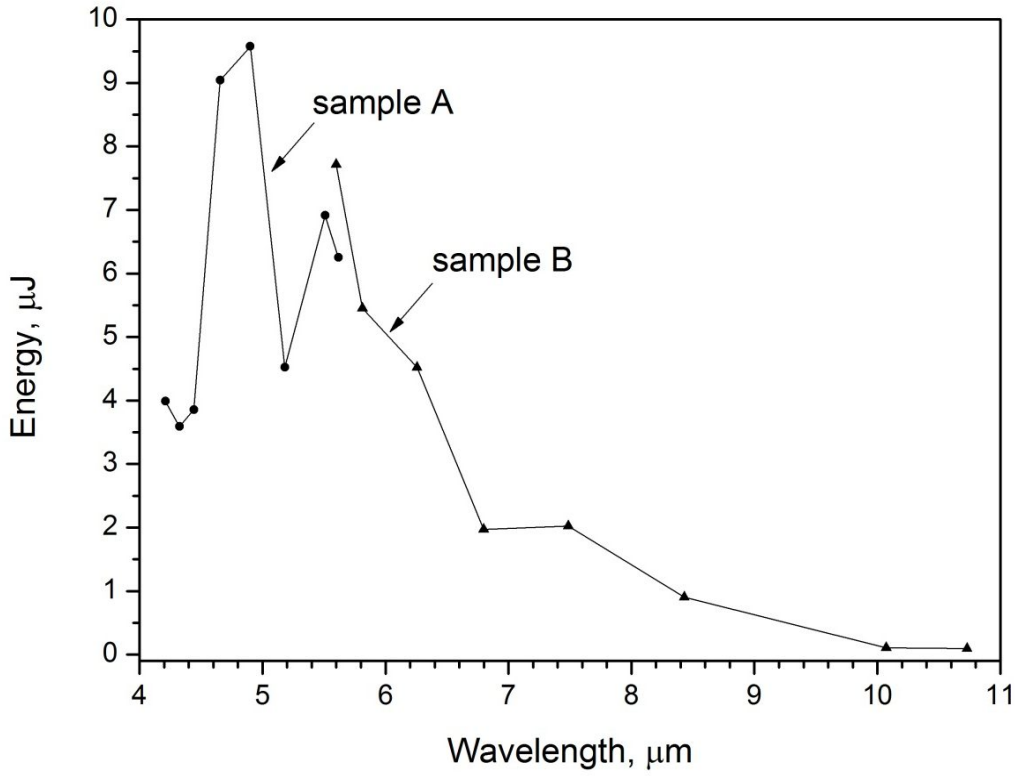

Figure 3. Idler energy versus idler wavelength: sample A (θ= 60°, φ= 0°); sample B (θ= 47°and φ= 0°)

4. ANALYSIS OF THE NH_3 ABSORPTION SPECTRUM

To demonstrate the feasibility of the OPO system for spectroscopic measurements and gas detection we took absorption spectra of NH_3 gas with distinct rotational–vibrational features in the mid IR. Ammonia in nitrogen mixture containing 0.1% was used as test gas. The used in this investigation PAD was 90 mm in length and had a fundamental resonance frequency of ~1800 Hz, and the quality factor was ~40. The PAD was filled with the test gas mixture via the gas purging. The pulse repetition rate of the pump laser was equal to the PAD resonance frequency. The OPO wavelength was continuously tuned in the spectral range of 9 - 10.8 μm (1110–926 cm^{-1}). The ammonia absorption spectrum was measured with the PAD. Data from the PD were used to normalize the PAD signals with respect to the idler energy. The normalized NH_3 absorption spectrum was recorded by the PC in real time.

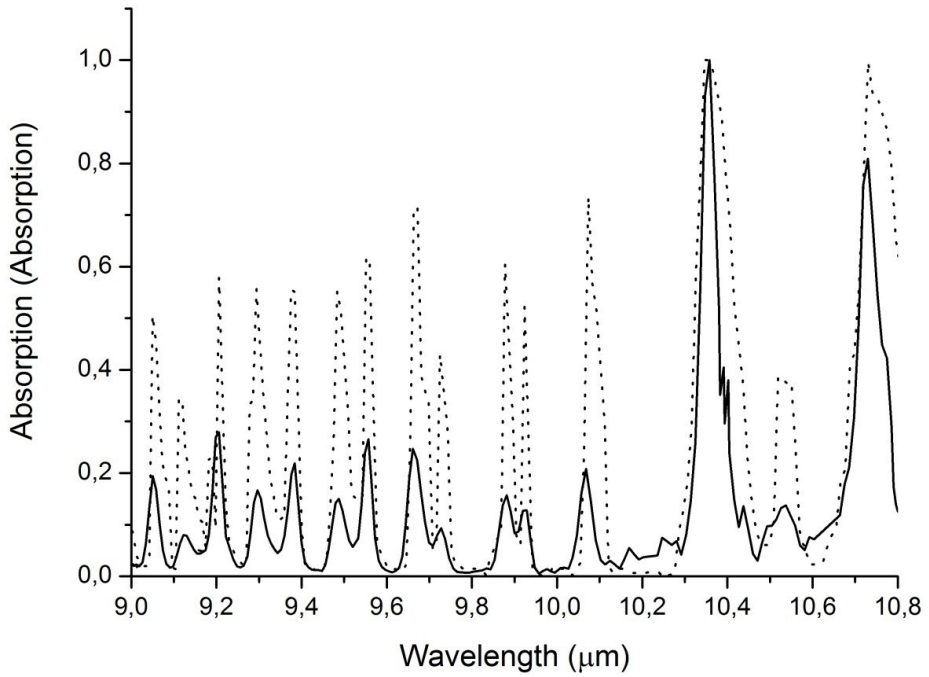

Figure 4. Absorption spectra of ammonia (gas mixture of 0.1% NH_3 in N_2). Solid line – experimental data, dashed line – data from NIST

Figure 4 compares NH_3 absorption spectrum obtained with our HGS OPO system and with NIST data (4 cm^{-1} resolution). As is seen in Fig. 3, the experimental absorption spectra and NIST data are with satisfactory agreement with each other.

5. CONCLUSIONS

In conclusion, developed OPO provides continuous wavelength tuning in the spectral range from 4.2 μm to 10.73 μm. Exceedingly wide wavelength tuning range was realized by precision linear switching of crystals and precision rotating of two HGS crystals. Using this developed OPO the ammonia absorption spectrum was investigated. The experimental absorption spectra and NIST data agree with each other. This device can be used for industrial, medical and other applications.

We propose a new conception of widely tunable nanosecond OPO based on two HGS crystals switching into the same cavity. Each crystal operates in the own spectral range, but the switching HGS crystal shifts wavelength tuning range to other spectral range.

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