Nonlinear optical frequency converters as an elemental base for IR lidars

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Results are presented of investigation and comparative analysis of parameters and characteristics of middle IR parametric frequency converters based on known crystals, $LiInS_2$ and $HgGa_2S_4$ crystals of limited occurrence, doped GaSe:In, and new mixed nonlinear $AgGa_{(1-x)}In_xSe_2$, $AgGaGeS_4$, $Hg_{(1-x)}Cd_xGa_2S_4$ crystals. Mobile lidar gas analyzers, supplied with the designed middle IR parametric frequency converters, are described. The results of monitoring of gas pollution in real atmosphere both under field conditions and industrial centers are presented as well.

Introduction

In few recent decades the methods and instrumentation of laser sensing of the atmosphere has received wide acceptance for both investigations in atmospheric physics and in remote monitoring of lower and upper atmospheric layers.[1] One can separate out two main problems that are solved most efficiently with lidars: (1) real time determination of content and composition of atmospheric aerosol; (2) real time monitoring of gaseous constituents of the atmosphere.

Monitoring of fine fractions of natural aerosol are usually carried out in a shortwave portion of the atmospheric transmission spectrum. Namely, in near IR, visible, UV spectral ranges up to the wavelength of 200 nm and shorter. These spectral ranges are covered by emission spectra of many lasers available, in particular, dye and Nd:YAG lasers with highly efficient (up to 80%) parametric frequency converters (PFC), excimer lasers with frequency shift via Stimulated Raman Scattering (SRS), tunable $Ti:Al_2O_3$ lasers, etc. The content of the coarse aerosol fractions of natural and anthropogenic origin are determined based on the measurement results obtained in longwave portion of the near IR and in the middle IR ranges at the wavelength up to 10 μm and longer. To record this type of aerosols, one can use powerful gas (CO_2 laser only) or chemical lasers operating in atmospheric transmission windows as well as Optical Parametric Oscillators (OPOs).

In monitoring the gas composition of the atmosphere with a high spatiotemporal resolution and sensitivity, the differential absorption method is more widely used. In this case the spectral range from 280 to 350 nm is the most suitable for determining concentrations of nitrogen oxides and other its compounds, as well as concentrations of O_3 and SO_2. Monitoring of methane average content along a chosen path may be realized using overtone absorption bands in near IR spectral range.

Measurements in the range from 2 to 14 μm, i.e., in the shortwave portion of the mid-IR range, have the best potentialities and give the best practical results in determining concentrations of many gaseous constituents of the atmosphere. It is precisely the spectral region where intense spectrally resolved absorption lines are and fine spectral structures of practically all atmospheric gases that may be used for measurements. To monitor one or another gas component, all lasers operating in the spectral range indicated are used. But there are no powerful and reliable narrow-band lasers that can be tuned over all spectral range considered. If there is a transition from shortwave portion of the mid-IR range to the range of 10 μm and farther when recording aerosol backscatter, so remote sensing requires the radiation pulse power of fractions, units, and even tens of Joules.

One of the most promising ways in solving this problem is using such traditional and efficient method of generation of radiation in new spectral ranges as parametric frequency conversion of radiation of lasers available by means of nonlinear crystal optics. This provides the possibility of tuning within wide spectral intervals by the converted monochromatic radiation. But the physical properties of such nonlinear crystals as Te, $CdGeAs_2$, $ZnGeP_2$, Tl_3AsSe_3, $AgGaSe_2$, GaSe, and CdSe, known from the end of 1960–1970s, were not clearly understood because of incompleteness of the crystal growth technologies. Therefore many types of PFCs based on these crystals have not been studied experimentally. Late in the 1970s the problem became urgent on investigation and creation of the middle IR PFC as radiation sources for gas analyzing lidars.

Below we discuss the results of the joint investigations carried out at the Institute of Optical Monitoring (Former Special Design Office “Optika,” then Institute of Design and Technology “Optika”) SB RAS, the Institute of Atmospheric Optics SB RAS, and Siberian Physical Technical Institute (SPhTI) at Tomsk State University obtained over recent 25 years on studying and development of mid-IR parametric frequency converters, as well as of lidar gas analyzers based on these PFC. Some measurement results are presented on studying gas composition of the atmosphere using frequency converted radiation. Finally the results are presented on investigation of the properties of poorly known, doped, and new nonlinear mixed crystals that can improve efficiency and reliability of the mid-

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IR PFC. These crystals give the chance to create a radiation source, emitting in the spectral range from 0.2 to 14 μm, for all-purpose gas-aerosol lidars based, for example, on Nd:YAG lasers.

1. Technique for estimating efficiency of parametric frequency converters

Now we show how we estimated the efficiency of PFCs using Second Harmonic Generation (SHG) as an example. In order to take into account the beams' thermal self-action, terms determining thermal effects have been introduced into the known system of reduced equations for complex amplitudes A_1 and A_2 of the pumping wave and second harmonic one, respectively.[2,3] The system itself had been supplemented with two-dimensional heat conduction equation. Finally the system of equations for calculating SHG efficiency took the form:

$$\frac{\partial A_1}{\partial z} - \frac{1}{2ik_1}\left(\frac{\partial^2 A_1}{\partial x^2} + \frac{\partial^2 A_1}{\partial y^2}\right) + \beta_1 \frac{\partial A_1}{\partial x} + \delta_1 A_1 + i\gamma_1 T A_1 = = -i\sigma_1 A_1^* A_2 \exp(-i\Delta k z),$$

$$\frac{\partial A_2}{\partial z} - \frac{1}{2ik_2}\left(\frac{\partial^2 A_2}{\partial x^2} + \frac{\partial^2 A_2}{\partial y^2}\right) + \beta_2 \frac{\partial A_2}{\partial x} + \delta_2 A_2 + i\gamma_2 T A_2 = = -i\sigma_2 A_1^2 \exp(-i\Delta k z),$$

$$\frac{\partial T}{\partial t} = \chi\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) + \frac{cn}{4\pi\rho C_p}\left(\delta_1 |A_1|^2 + \delta_2 |A_2|^2\right).$$

Here k_1 and k_2 are the wave numbers of the pump and SH waves; $\Delta k = k_1 - 2k_2$ is the wave detuning; $\beta_{1,2}$, $d_{1,2\mathrm{eff}}$, $\delta_{1,2}$, and $\sigma_{1,2} = 4\pi k_{1,2}\, d_{1,2\mathrm{eff}}/n^2(\omega, 2\omega)$ are the cut-off angles, efficient nonlinear susceptibilities, coefficients of linear optical losses and nonlinear matching, respectively; T is the crystal temperature excess over the ambient one; $\gamma_{1,2} = k_{1,2}(\partial n_2/\partial T)$ are the coefficients accounting for thermal self-action; $\chi = \kappa/(\rho C_p)$ is the temperature conductivity coefficient; κ is the thermal conductivity coefficient; ρ is the density; and C_p is the crystal specific heat capacity.

Numerical simulation was carried out with the account for the initial and boundary conditions for two pumping modes: single pulse and pulse-periodic ones. The shapes of radiation pulses and intensity distribution in the beam cross section are assumed to be rectangular and Gaussian for both cases, i.e., with and without the account for the process of establishment of the temperature field inside the crystal. To solve this system, the numerical fast Fourier transform algorithm was applied. It saves the calculation time as compared with the alternative finite difference methods.[4]

It follows from the tentative estimations that at SHG of single pulses, the $ZnGeP_2$ crystals with the length less than 2 cm are second only to $CdGeAs_2$. Other nonlinear crystals, that have length of many centimeters, outperform them by maximum 1.8 times. When operating in a pulsed mode the following maximum efficiencies are achieved: 57% in 2-cm $ZnGeP_2$ crystal (SH has an average power of 16 W) at pulse power of 60 mJ, pulse repetition rate of 300 Hz, pulse duration of 100 ns, and wavelength of 9.3 μm. At the same conditions and 9-cm crystal length the efficiencies are 42% (22 W) for $AgGaSe_2$ and 56% (22 W) for Tl_3AsSe_3.

Note that $CdGeAs_2$ operates at cryogenic temperature that results in additional losses that are not taken into account. The determined temperature dependences of phase matching and estimated changes of phase matching conditions at PFC of powerful radiation allowed us to optimize the PFC efficiency by choosing both an optimal crystal temperature and pumping radiation direction.[9] The offbeat estimations have made a basis for experimental investigations.

2. Some experimental results

By now $ZnGeP_2$ crystal is one of the most attractive crystals for applied nonlinear optics in the mid-IR range. There is very interesting situation with this crystal. The $ZnGeP_2$ compound synthesis was made in Leningrad Physical Technical Institute (LPhTI) in 1963 and it was firstly mentioned in Ref. 5. The crystal samples produced in 1969 allowed one to investigate their optical properties. Possibilities of using this crystal in nonlinear optics were studied in 1971.[6] It turned out that $ZnGeP_2$ crystal has the third in magnitude figure of merit $M = = d^2/n_1 n_2 n_3$ (M is proportional to the potential PFC efficiency, here d is the nonlinear susceptibility coefficient of the second order, $n_{1,2,3}$ are refraction indices for interacting waves). But this crystal is the first by this parameter among those nonlinear crystals that are transparent in both middle and near IR spectral ranges.

On the other hand the peculiarities in transparency spectrum (coefficient of optical losses $\delta = 0.3–0.9\ \mathrm{cm}^{-1}$ in the region of 9–11 μm and δ ranges from 10–20 to $50\ \mathrm{cm}^{-1}$ and higher near the so-called shortwave absorption "shoulder" at 0.7–2.5 μm), thermal properties, and dispersion dependences of $ZnGeP_2$ crystal showed that this crystal is inappropriate for PFCs development at all and, in particular, for parametric frequency conversion of CO_2 laser radiation. Two first experiments proved this statement because the PFCs realized had extremely low efficiencies. These PFCs were realized for submillimeter wave oscillator by means of difference frequency generation of various pairs of CO_2 laser emission lines and for up-conversion of the emission of the same laser.[7] For two decades $ZnGeP_2$ crystal did not attract attention of foreign researchers[7] and only once was mentioned by Russian scientists[8] showing poor thermal properties and low damage threshold.

The works on transferring the $ZnGeP_2$ crystal growth technology from LPhTI to Siberian Physical Technical Institute (SPhTI) and then to Joint Institute of Atmospheric Optics (Institute of Atmospheric Optics SB RAS and Special Design Office "Optika") were completed in 1979. This allowed us to carry out many-year complex investigations. The results obtained turned out to be encouraging for creation of a PFC based on $ZnGeP_2$ crystals.$^{9-11}$ Simultaneously production of GaSe and some other crystals were mastered. The complex investigations of optical properties of a number of new nonlinear crystals have been enlarged as well.

The main results obtained are the following. It was shown for the first time, that among crystals capable of working in mid-IR range $ZnGeP_2$ crystals have maximum damage threshold that nonlinearly grows as CO_2 laser pulse duration decreases. The method of chemical-dynamic polishing suggested increased damage threshold by 10–12% more. The thermal conductivity measured (0.36 W/(cm·K)) turned out to be surpassing the one for other crystals by 2.2 times (GaSe), 33 times ($AgGaSe_2$), and up to 180 times (Te), and the thermal capacity of $ZnGeP_2$ crystals is 1.3 (GaSe) to 5.3 (CdSe) times greater. It was found that $ZnGeP_2$ crystal ranks 9.3 times below $CdGeAs_2$ crystal in figure of merit but surpasses it 5.4 times in thermal conductivity and 1.4 times in thermal capacity. All this led us to conclusion that $ZnGeP_2$ crystal is quite competitive for parametric frequency conversion of all CO_2 lasers. $ZnGeP_2$ crystal surpassed all nonlinear crystals known by the time of measurements within the maximum transparency window. An efficiency of PFC of Nd:YAG and holmium lasers radiation is limited by shortwave absorption “shoulder.” An effect of optical absorption anisotropy, found in this region for the first time, showed that efficiency of PFC of the radiation from this spectral range is severely underestimated. The estimations have been made for unpolarized radiation, while optical losses for *e*-wave (exactly *e*-wave has the highest frequency when interacting in positive crystal) turned out to be at least 3–8 times lower than for *o*-wave.

The first results on second harmonic generation[12] have shown rather high efficiency of almost 10% and pointed to the necessity of long-term verification of these experimental results. 1988 have completed investigations of PFCs of radiation of practically all known lasers, operating in the spectral region considered. Investigation results on SHG are presented in Table 1, while the results on other frequency converters are in Table 2.

Table 1. Efficiency of realized second harmonic oscillators

Crystal	Pumping laser	Parameters of pumping radiation			External (internal) η, %
		λ, μm	I, W/cm^2	τ, s	
$ZnGeP_2$	cw CO_2	9.2–10,8	$2\cdot10^5$	–	10^{-2}
	Q-switched CO_2	9.2–10.8	$(0.5–1.0)\cdot10^5$	$10^{-4}–10^{-2}$	5
	Q-switched CO_2	4.3-μm band	–	$(1.5–3.3)\cdot10^{-7}$	8.4 (10.1)
	Q-switched CO_2:Xe	9.55	$0.5\cdot10^6$	10^{-7}	6.8
	Mini TEA CO_2	9.2–10.8	$5\cdot10^7$	$4.5\cdot10^{-8}$	6*; $\overline{P}$ = 0.22 W
	TEA CO_2	9.2–10.8	$6\cdot10^7$	$(1.7–2)\cdot10^{-7}$	9.3*
	SH of TEA CO_2	4.65	$3.5\cdot10^7$	10^{-7}	6.8
	–“–	9.63	$6\cdot10^7$	$5\cdot10^{-8}$	30
	High pressure TEA CO_2	9.17–9.7 and 10.15–10.8	$8\cdot10^7$	$(4–5)\cdot10^{-5}$	0.9*
	TEA CO_2:CO-mixture laser	9.2–10.8	–	$(0.5–10)\cdot10^{-6}$	0.1*
		5.3–6.1		$(4–5)\cdot10^{-5}$	0.1*
	Nanosecond hybrid CO_2	9.28	10^9	$2\cdot10^{-9}$	49 (83.5)
	–“–	10-μm band	10^9	$2\cdot10^{-9}$	17
	SH of nanosecond hybrid CO_2	4.64	$0.3\cdot10^9$	~ $2\cdot10^{-9}$	14 (22)
	cw CO	5.3–6.1	$2.5\cdot10^5$	–	0.5
	Q-switched CO	5.3–6.1	–	$4.5\cdot10^{-5}$	3.1
	DF	3.6–4.0	$3\cdot10^7$	$1.5\cdot10^{-7}$	6.2 (11.8)
Te	TEA CO_2	9.3	$3.5\cdot10^7$	10^{-7}	0.47 (3.4)
$CdGeAs_2$	cw CO_2	10.6	$1.5\cdot10^3$	–	0.17
	TEA CO_2	9.2–10.8	$2\cdot10^7$	$2.0\cdot10^{-7}$	0.3
	Pulsed NH_3	11.7	$3\cdot10^7$	$1.5\cdot10^{-7}$	2 (5.2)
	Nanosecond CO_2	9.28	10^9	$2\cdot10^{-9}$	3.1
Tl_3AsSe_3	Q-switched CO_2	10.6	$2\cdot10^6–2\cdot10^7$	$10^{-2}–10^{-3}$	$2.1\cdot (10^{-3}–10^{-2})$
	TEA CO_2	9.3	$3.5\cdot10^7$	$1.5\cdot10^{-7}$	2.3
$AgGa_xIn_{1-x}Se_2$	Pulsed CO_2:XE	9.55	$0.5\cdot10^6$	10^{-7}	10.9
	TEA CO_2	9.28–9.64	–	–	3.7
$AgGaSe_2$	cw CO_2	9.28–9.66	–	–	SHG recording
	Pulsed CO_2:XE	9.55	$0.5\cdot10^6$	10^{-7}	4.1
	TEA CO_2	9.64	$3\cdot10^7$	$5\cdot10^{-7}$	1.5
GaSe	Pulsed CO_2:XE	9.55	$0.5\cdot10^6$	10^{-7}	0.2
	TEA CO_2	9.3	$3\cdot10^7$	$5\cdot10^{-7}$	0.35

Note. Designations: cw is continuous wave laser; * (asterisk) means energy conversion efficiency; $\overline{P}$ is SH mean power.

Table 2. Oscillators of combination frequency, higher harmonics, and parametric luminescence that have been realized

PFC type	Pumping laser	Parameters of pumping radiation			External (internal) η, %
		λ, μm	I, W/cm^2	τ, s	
SFG in $ZnGeP_2$	cw CO and CO_2	5.3–6.1 and 9.2–10.8	$2\cdot10^5$	–	0.25 mW,
	Q-switched CO_2	4.3;10.4 (second sequence band)	–	$(1.5–3)\cdot10^{-7}$ and $6\cdot10^{-7}$	4 W peak (20% from 4.3 μm)
	Combined on $CO:CO_2$ mixture	5.3–6.1 and 9.2–10.8	10^7	$5\cdot10^{-5}$	10^{-2} from emission of mol. CO
Up-conversion in $ZnGeP_2$	Q-switched Nd:YAG + Q-switched CO_2	1.064 10.51	$3\cdot10^5$ $8\cdot10^5$	$5\cdot10^{-6}$ $5\cdot10^{-6}$	2
SFG in $CdGeAs_2$	TEA CO_2 and NH_3	9.2 and 11.7	$3\cdot10^7$	$1.7\cdot10^{-7}$ and $1.5\cdot10^{-7}$	Recording of generation
SFG in CdSe	$Er^{3+}:CaF_2$, Er^{3+}:YAG and cw CO_2	2.76; 2.94 and 10.6	$8\cdot10^6$; $8\cdot10^6$ and $3\cdot10^2$	$3\cdot10^{-8}$; $3\cdot10^{-8}$	≤ 12
DFG in $ZnGeP_2$	$Er^{3+}:CaF_2$, Er^{3+}:YAG and cw CO_2	2.76; 2.94 and 10.6	$8\cdot10^6$ $8\cdot10^6$ $3\cdot10^2$	$3\cdot10^{-8}$; $3\cdot10^{-8}$ –	3
	Double-frequency TEA CO_2	9.2–10.8	$5\cdot10^6$	10^{-7}	≈ 2 W, peak, $\Delta\lambda = 0.15$ μm
Cascade FHG in $ZnGeP_2$	Hybrid CO_2	9.28	10^9 and	$2\cdot10^{-9}$	1.5
	TEA CO_2	9.2–10.5	$6\cdot10^7 – 0.3\cdot10^9$	$(1.7–2.0)\cdot10^{-7}$	1
PL in $ZnGeP_2$	Er^{3+}:YSGG	2.79	10^{10}	10^{-10}	10 (temperature tuning)
PLG in CdSe	$Er^{3+}:CaF_2$ + 1 Cascade amplifier	2.76	$\le 10^7$	$3\cdot10^{-8}$	≤ 10
PLG in CdSe	$Dy^{2+}:CaF_2$ + 2 Cascade amplifiers	2.36	$\le 10^7$	$3\cdot10^{-8}$	≤ 10

Note. SFG is the sum frequency generation, DFG is the difference frequency generation, FHG is the fourth harmonic generation, PL is the parametric luminescence, and PLG is the parametric light generation.

PFC of pulse-periodic Q-switched CO_2 laser operating at fundamental, second sequence, and 4.3-μm emission bands, is of particular interest.[13,14] Generation of harmonics and mixing emission lines of all bands allowed us to create a coherent radiation source that emits in the range from 2.15 to 11.0 μm with a density of resolved emission lines up to 10^{-3} cm^{-1}.

When used in a lidar gas analyzer in the near-ground atmosphere, such a source, having a radiation line width no more than $2\cdot10^{-3}$ cm^{-1}, has potentialities similar to those of a frequency-tuned laser. The most frequency conversions were carried out with high (for the lasers not adapted for nonlinear optics problems) or record efficiencies. An efficiency of 80% has been experimentally demonstrated for frequency doubling a 2-ns duration pulse.[15] This is the absolute record in the efficiency of mid-IR PFCs for the last 13 years. Success of IAO SB RAS and IOM SB RAS in investigating PFC gave a chance to develop and produce the first multipurpose model and the first in the world pilot series of mid-IR PFC. Development of differential absorption lidars using these PFCs was started at IAO SB RAS.

3. Application in lidar gas analyzers

The first known differential absorption lidar system operating in the middle IR spectral range was created and tested in 1977–1978 (Ref. 16). PFC based on CaSe crystal pumped with Er^{3+}:YAG (2.96 μm) and cryogenic $Dy^{2+}:CaF_2$ (2.36 μm) lasers (each laser had two amplifying cascades) was used as a radiation source. This source operates in ranges from 2.8 to 4.2 and from 7.5 to 13.7 μm. Extremely short PFC lifetime (usually no longer than some hundreds of emission pulses) caused by the proximity of the crystal damage threshold and oscillation threshold stimulated investigations presented in this work. Next system based on two CO_2 lasers with PFC made from $ZnGeP_2$ crystals have been installed in a van and successfully tested in 1984–1985 in the USSR and Bulgaria.[17]

This system is a trace gas analyzer operating with the use of retroreflector. The real-time measurements of C_2H_4, water vapor, NH_3, and O_3 concentrations were carried out at the fundamental wavelength. In addition, the measurements of CO concentration were carried out at the SH wavelength with a sensitivity sufficient for CO background content monitoring accurate to ppb level. Using this trace gas analyzer we determined second, minute, hour, and diurnal behavior of CO concentration. The measurements were carried out at SH of $9R(18)$ line that coincides with $P(2)$ absorption line of CO fundamental band and at $9R(20)$ line lying off this line.

Later, the measurements were carried out under different conditions, including those in mountains and in rural areas. They made it possible to enlarge the measurement time up to weeks and even months.[18] Measurements of NO concentration at SH wavelength and N_2O concentration at sum frequency of 9*R*(40) and 9*R*(18) lines, emitted by two CO_2 lasers, were carried out a bit later.[19] The possibility of measuring CO_2 and NO_2 content has been demonstrated in laboratory.

Next version of the trace gas analyzer had three tunable lasers, namely, two CO_2 and CO lasers, with a set of PFCs.[20] It was shown in measurements that the path length of 20 m is sufficient for monitoring CO background content by virtue of its high content in the atmosphere and high absorption coefficient ($29.7\ cm^{-1}\cdot atm^{-1}$). This circumstance allowed us to measure CO concentration using low-power Q-switched CO_2 laser (peak power is 1–3 kW) and SHG with the efficiency of 5%. In this case topographic targets were used as retroreflectors. As the distance to the target was up to 500 m and InSb photodiodes were applied, signal-to-noise ratio achieved 100 (Ref. 21).

Experience in working with remote objects created a ground for development lidars based on powerful TEA CO_2 lasers that provided recording aerosol backscatter. Another reason was an increase in lidar potential resulting from the increase in detectors' sensitivity at the frequency of CO_2 laser radiation converted with PFC's into shortwave spectral region. Actually, even at a relatively low SHG efficiency of the order of 10–20%, the energy losses are compensated by an increase in the sensitivity of 5-μm detectors based on InSb. In 1993–1996 a lidar complex was created that included a dual-mode lidar (operating both in aerosol backscatter mode and using a topographic target) and modernized version of trace gas analyzer. Both parts of the lidar complex are completed with PFC.

The lidar operating range is 10–15 km when working with topographic targets and 5 km when recording aerosol backscatter. In the first case when using targets that are 3 km away from the lidar, the signal-to-noise ratio of up to 10000 was obtained in one pair of shots. In the second case 2D maps of C_2H_4 spatial distribution were obtained.[22] The lidar complex has been successfully tested in Republic of Korea.

The experience obtained in working with the lidar gas analyzers has shown that in order to improve their potentialities, an interest is in detailed investigation of the properties of poorly studied crystals and in improving parameters of known and new nonlinear crystals.

4. New promising nonlinear crystals

$LiInS_2$ crystals

$LiInS_2$ semiconductor nonlinear crystals are poorly studied despite the fact that they have wide transparency spectrum, which spans visible, near IR, and middle IR spectral regions, quite high nonlinear susceptibility, and quite reasonable birefringence. These crystals can not have pretensions to a leadership in any spectral region because they rank below oxide crystals in the visible and near IR spectral regions in damage threshold and below many crystals in the middle IR spectral region in nonlinear susceptibility coefficient. Recent progress in $LiInS_2$ crystal growth technology has stimulated investigations of their physical properties and possibility of using these crystals in lidars.[23]

The transparency band of uncolored crystal 3.6 mm long is from 0.4 to 12.5 μm at a level of 0.1. Its dispersion properties provide a possibility of creating a middle IR parametric light oscillator (PLO) pumped with Nd:YAG laser as well as copper-vapor or dye lasers. It was shown for the first time that phase-matching conditions of *fsf*- and *sff*-types are fulfilled in the *xy* plane for different PFCs (SHG, SFG, and DFG) of femtosecond pulses in a wide wavelength range (from 1.2 to 11.5 μm). Note that at the present time $LiInS_2$ crystals are the only crystals suitable for SHG of 3-μm femtosecond laser radiation. Nonlinear susceptibility turned out to be by 80% lower than known values.[23] The damage threshold has been determined for 36-ns pulses of TEA CO_2 laser. It is equal to 180 MW/cm^2. It is obvious that relatively poor nonlinear properties of these crystals as compared to known data will limit their use in lidar systems.

$HgGa_2S_4$ crystals

Progress achieved in the crystal growth technology of another poorly studied crystal, $HgGa_2S_4$, allowed detailed investigations to be made of optical properties of two crystal phases (yellow and orange) having relatively high optical quality. An experiment on SHG of TEA CO_2 laser radiation was carried out as well. The shortwave boundary of its transparency spectrum is near 490 nm for yellow phase and near 507.5 nm for orange one at the zero level. Longwave boundaries for both phases did not differ and were near 15.5–16 μm at the same level. It should be pointed out that at the wavelengths of 9-μm CO_2 laser emission band and its second harmonic losses caused by phonon absorption are comparable or less than those for $ZnGeP_2$ and $LiInS_2$ crystals.

Analysis of phase-matching conditions has shown that it is possible to generate a second harmonic of 9-μm CO_2 laser emission band and to develop a middle IR parametric light oscillator pumped with Nd:YAG, $Ti{:}Al_2O_3$, and copper-vapor lasers. First type SHG has been experimentally investigated for TEA CO_2 laser emission line with the wavelength of 9.55 μm. Both calculated and experimentally obtained phase-matching angles were in a good agreement for the orange crystal phase, while for the yellow phase experimental values were a bit lower than the calculated ones. Estimations of potential efficiency have shown that $HgGa_2S_4$ crystals will outperform the known crystals in SHG of Ho:ILF laser radiation and 9-μm CO_2 laser emission band at similar pumping intensity.

As follows from the physical properties determined, in competition between PFC based on $ZnGeP_2$ and

$HgGa_2S_4$ crystals the relationship between their damage thresholds is the decisive factor. Comparative measurements of the damage threshold under exposure to TEA CO_2 laser that were thoroughly carried out for these two and other ten nonlinear crystals have yielded the following results. $HgGa_2S_4$ crystal (orange and yellow phase) has damage threshold, respectively, 2.1 and 2.2 times greater as compared with that of $ZnGeP_2$ crystal. Such an excess is characteristic for poorly studied and new mixed nonlinear crystals transparent in visible and middle IR spectral regions. $HgGa_2S_4$ crystals have more than 5-fold advantage over $ZnGeP_2$ crystals in such a parameter as product of damage threshold by figure of merit that is proportional to SHG efficiency. This fact clearly demonstrates that this crystal is a candidate for nonlinear optics in the middle IR region. It was shown that among known crystals this crystal is most efficient for the development of middle IR PFC pumped with Nd:YAG laser. Advantage in SHG of 9-μm CO_2 laser emission band achieves 5.5-fold value.

GaSe and GaSe:In crystals

Extremely wide transparency range (0.65–19.0 μm), very large birefringence $B = 0.375$, and relatively high nonlinear susceptibility d_{22} ranging, according to data borrowed from different authors, from 23 to 54.4 and even to 75 pm/V (Ref. 25) make it possible to realize highly efficient PFCs based on GaSe crystals for all known lasers operating in near and middle IR spectral region. High thermal conductivity, equal to 0.162 W/(cm·deg), in the layers' plane, simple growth technology, and low price also favor the creation of such PFCs. The possibility should be emphasized of creating PFCs for such widely spread lasers as Nd:YAG lasers including development of optical parametric oscillators based on these lasers. However these crystals have not received wide acceptance in applied devices because they have a drastic disadvantage, namely, layering. It caused pronounced mechanical and thermal anisotropy, made impossible mechanical treatment of working surfaces and manufacturing optical elements with arbitrary orientation.

For this reason the experiments carried out have shown not very good results in many cases for SHG of CO_2 laser radiation, parametric superluminescence, and parametric light generation, although the frequency converted spectrum overlapped extremely wide spectral range from 3.3 to 19.0 μm.[26] The situation has been appreciably cleared up in Ref. 25 and in our later investigations.[27] High natural nonlinearity ($d_{22} = 70$ pm/V) of these crystals turned out to be hidden by bad cleavage. Doping by In (0.3–1.0%) made it possible to change all properties drastically. Microhardness increased by an order of magnitude. It allowed to treat the GaSe crystals, including polishing, by means of ordinary methods. Eight-fold difference between thermal conductivity in the layers and perpendicular to them decreased by almost 4 times. All this means that doped GaSe crystals can become a top-level crystals for many mid-IR PFCs outperforming the $ZnGeP_2$ crystals.

$AgGa_xIn_{1-x}Se_2$ crystals

An efficiency of nonlinear crystals for PFC of laser radiation depends, in a high degree, on phase-matching conditions for interacting waves. As a rule, phase-matching angles differ from optimal and noncritical 90° direction. The first fact decreases d_{eff}. The second one leads to walk-off of the interacting beams because of birefringence, limits maximum length of crystals used, and gives additional decrease in the efficiency. As an alternative to the known nonlinear crystals we have studied experimentally PFC in mixed $AgGa_xIn_{1-x}Se_2$ crystals. These crystals are $AgGaSe_2$:$AgInSe_2$ solid solutions.[28] Dispersion curves and Sellmeier coefficients determined for various x values make it possible to choose such an In content that provides for fulfillment noncritical 90° phase-matching for SHG of all CO_2 laser radiation spectrum or other PFCs. Superiority of $AgGa_{0.6}In_{0.4}Se_2$ mixed crystal over $ZnGeP_2$ and $AgGaSe_2$ crystals turned out to be 10.9:4.1:6.8% that is rather close to the expected results. This proves that $AgGa_xIn_{1-x}Se_2$ crystal offers promise for PFCs and we also need to find new mixed crystals.

$AgGaGeS_4$ ($AgGaS_2$:GeS_2 solid solution) and $Cd_{(0.4)}Hg_{(0.6)}Ga_2S_4$ ($HgGa_2S_4$:$CdGa_2S_4$) mixed nonlinear crystals

These crystals[29] are among few crystals transparent in both mid-IR and at the wavelengths of 1 μm and shorter. For $AgGaGeS_4$ 10×15×2.1-mm specimen the shortwave boundary of transparency spectrum is near 440 nm and longwave one is near 14 μm.[30] Optical losses for the wavelengths of CO_2 laser 9-μm band are a bit lower than ones for $ZnGeP_2$ and $LiInS_2$ crystals. It was found that phase-matching conditions are fulfilled for $e \to oo$ interactions in XZ plane with $d_{eff} = d_{32} \sin\theta$ and in YZ plane with $d_{eff} = d_{31} \sin\theta$. They are also fulfilled for $o \to ee$ interactions in XY plane with $d_{eff} = d_{31} \sin^2\varphi + d_{32} \cos^2\varphi$, where $d_{32} = 8$, and $d_{31} = 12$ pm/V, respectively; θ and φ are spherical coordinates. The spherical coordinate axes are related to crystal system axes. Comparing $AgGaGeS_4$ and $ZnGeP_2$ crystals, we can say that the nonlinear coefficients for the first one are much lower but damage threshold is 1.7 times higher. For SHG of CO_2 laser radiation $AgGaGeS_4$ crystal outperforms $ZnGeP_2$ crystal by a factor 1.4 because of small refraction indices and closeness of phase-matching angles to the optimal one (noncritical 90° angle).

Thus, the linear and nonlinear characteristics determined have shown that mixing GeS_2 and $AgGaS_2$ crystals leads to widening the transparency range and increasing birefringence and damage threshold. The birefringence becomes large enough for phase-matching fulfillment and creation of a Nd:YAG-laser-pumped PFC for 1.1–11.5 μm spectral range and copper-vapor-laser-pumped PFC for 4.0–11.5 spectral range.

Transparency spectrum of 6.5×8×2.1-mm $Hg_{0.65}Cd_{0.35}Ga_2S_4$ mixed crystal having $42m$ point symmetry is close to one of $HgGa_2S_4$ by its potentialities in realization of a PFCs of different types.[28] The damage threshold for CO_2 laser pulses is 1.9 times higher than that of $ZnGeP_2$ crystal. The parameters and characteristics determined for this mixed crystal allow us to say that this crystal holds the greatest promise for overlapping mid-IR range by means of frequency conversion of Nd:YAG laser radiation and radiation of other lasers operating in the near IR and visible spectral ranges.

Conclusion

The investigations carried out in 1976–1978, enabled us to design a prototype of a middle IR differential absorption lidar based on parametric light oscillator with CdSe nonlinear crystal pumped with Er^{3+}:YAG and Dy^{2+}:CaF_2 laser radiation.

Physical properties of nonlinear crystals working in the mid-IR investigated jointly at IOM SB RAS, IAO SB RAS, and SPhTI at TSU allowed us to develop frequency converters for almost all lasers emitting in the middle and near IR spectral ranges. These frequency converters have rather high efficiencies, and 80-% efficiency of second harmonic oscillator of nanosecond TEA CO_2 laser is the highest in the middle IR spectral range. The demonstrated $ZnGeP_2$ crystal superiority allowed us to make prototypes and then make pilot series of mid-IR frequency converters named Spektr. These frequency converters have been used in mobile lidar gas analyzers based on the most sensitive optical method, namely, differential absorption method. Application of these frequency converters removed restrictions on the number of atmospheric gases to be monitored. The lidars have been successfully field tested in Russia and abroad.

Investigations of optical linear and nonlinear properties, as well as physical characteristics of $LiInS_2$ and $HgGa_2S_4$ crystals, doped GaSe:In, and new mixed nonlinear $AgGa_{1-x}In_xSe_2$, $AgGa_{1-x}Ge_xS_4$, and $Hg_{(1-x)}Cd_xGa_2S_4$ crystals have shown their advantages over the known ones. The dispersion characteristics of these crystals provide for frequency conversion (within transparency spectrum) of mid-IR lasers radiation as well as the development of parametric oscillators pumped with Nd:YAG and Ti:Al_2O_3 laser radiation. It is possible to use other lasers emitting in the near IR and visible spectral ranges including copper-vapor laser. The damage threshold is 1.5 to 3 times higher than that for known crystals. This results in the fact that, in combination with other parameters, the efficiency of CO_2 laser radiation conversion with $HgGa_2S_4$ crystals is 5.5 times higher than that with $ZnGeP_2$ crystals. Using PFCs based on new nonlinear crystals that convert Nd:YAG laser radiation into middle IR spectral range in combination with well known PFCs based on LBO, BBO, KTA, KTP, and CLBO crystals that convert their radiation into visible and UV spectral ranges makes it possible to develop superwideband coherent radiation sources with a radiation tunability spectrum from 0.2 to 14–15 μm. Such sources may be used in multi-purpose lidar gas analyzers. The possibility has been shown of using $LiInS_2$ crystals for frequency conversion of femtosecond laser radiation of 1.2 to 11.5 μm range. It is worth noting that among known crystals $LiInS_2$ crystal is the first one suitable for frequency conversion of 3-μm femtosecond laser radiation.

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