Conversion of CO$_2$ laser radiation into far IR spectral range with a ZnGeP$_2$ crystal

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All possibilities of CO$_2$ laser frequency conversion into the far infrared (FIR) and super-high frequency (SHF) ranges have been analyzed on the basis of systematized data on linear optical properties of ZnGeP$_2$ single crystals for the first time. The coefficients of dispersion Sellmeier equations for FIR range have been determined. Phase-matching curves and phase-matching angular widths for both direct and backward waves have been calculated. A principle possibility of applying the emission converted to control HF, NH$_3$, HCl, HOCl, OH, and HBr content in gas mixtures is shown.

As known, the far infrared (FIR), or submillimeter, spectral range contains resolved rotational absorption spectra of many molecular components of the atmosphere. Therefore, this spectral range is very attractive for gas analysis and spectroscopy of dipole and nonpolar liquids, as well as solid bodies. On the other hand, the problem on creation of narrow-band sources of tunable radiation with a sufficiently high output power for this spectral range has been solved for a long period. The FIR gas lasers have only separate fixed wavelengths. It is possible to cover the 0.2–10 mm range with the use of backward-wave tubes, but it does not permit one to solve all the problems because these tubes are very technically complicated and have low output power (0.5–40 mW). Besides, spectrometers with backward–wave tubes require additional units to control the amplitude, phase, and polarization, as well as to determine the spectral parameters. High-sensitive detectors are also needed. As a result, the spectrometers with backward-wave tubes are still quite specific laboratory devices having rather high price.

In 1972 narrow-band ($\Delta\nu = 10^{-3}$ cm^{-1}) tunable generation in 70–110 μm spectral region with an output power of 1.7 μW had been reported for the first time. This generation was realized by means of a nonlinear-optics technique involving phase-matching. The frequencies of two discrete tunable CO$_2$ lasers were mixed in a ZnGeP$_2$ single crystal. It should be especially noted that the conversion was realized without cryogenic instrumentation and superconductor magnets, what is traditional for this research. The replica of this experiment enabled obtaining radiation pulses in the FIR with the power above 1 W (Ref. 2 and 3).

Such a source has a number of peculiarities. First, it provides for obtaining a dense, with the step of 10^{-3} cm^{-1}, overlapping throughout the entire FIR range by difference frequency generation of two low-pressure

CO$_2$ lasers or hybrid CO$_2$ lasers. Second, it does not require additional units to form and control the spectral width of a line. This line is a laser line broadened by a factor of $\sqrt{2}$. The latter one is, in its turn, determined by the laser physical parameters and equal to $\sim 2\cdot10^{-3}$ cm^{-1} for the lasers without frequency selection. When stabilizing the laser amplitude and frequency and using the mode selection,[4] the line width can be reduced to 10^{-6} cm^{-1}. Third, it does not require any special device to control the spectral position of emission lines because they are well known for the above-mentioned lasers and can be easily controlled with a diffraction grating and a stepper motor, and, if necessary, with a piezo-corrector. As a whole, such a sibmillimeter source, around which spectrophotometers can be built up, looks like a simple, relatively cheap, and reliable instrument.

In spite of the above-indicated attractive features, the sibmillimeter radiation source considered is still poorly studied both theoretically and experimentally.

The goal of this work was to systematize the data on optical properties of ZnGeP$_2$ crystals available for the IR and FIR spectral ranges as well as to evaluate the potentialities of CO$_2$ lasers frequency conversion into FIR for both earlier realized and all other possible types.

The real and imaginary parts of the dielectric constant of ZnGeP$_2$ single crystals have been determined for both ordinary and extraordinary IR and SHF waves using a standard technique based on the data on transmission and reflection coefficients of a 405-μm ZnGeP$_2$ plate. Backward-wave spectrometer "EpsilonB has been used in the submillimeter range.[5] Spectral dependences of the refractive indices of ordinary (o) and extraordinary (e) waves in the middle and far IR regions are approximated by the dispersion Sellmeier equations that have the form

$$n_{o,e}^2 = A_{o,e} + B_{o,e}\,\lambda^2/(\lambda^2 - C_{o,e}) + D_{o,e}\lambda^2/(\lambda^2 - E_{o,e}),$$

where λ is the wavelength in μm.

Table 1. Sellemier constants for the IR and FIR regions.

ZnGeP$_2$		A	B	C	D	E
IR	o	4.5069	5.2334	0.1343	1.7367	750
(1–12) μm	e	4.6613	5.3153	0.1430	1.6982	750
FIR	o	10.4810	0.9340	1811.0	0	–
(0.1–8) μm	e	11.1790	0.4330	2952.0	0	–

The Sellmeier constants obtained by us for FIR and those for IR borrowed from Ref. 6 are presented in Table 1. The typical dependences of absorption coefficients for IR region can be found in Ref. 3, and those for FIR are presented in Fig. 1.
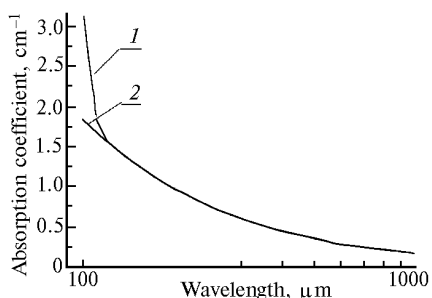

Fig. 1. Spectral dependence of the absorption coefficients for ordinary (*1*) and extraordinary (*2*) waves in the FIR spectral range.

The calculated phase-matching curves show a possibility of realizing collinear interaction of four types:

$$\mathbf{k}_{1e} - \mathbf{k}_{2o} = \mathbf{k}_{3o}, \quad \mathbf{k}_{1e} - \mathbf{k}_{2o} = \mathbf{k}_{3e};$$
$$\mathbf{k}_{1o} - \mathbf{k}_{2e} = \mathbf{k}_{3e}, \quad \mathbf{k}_{1o} - \mathbf{k}_{2e} = \mathbf{k}_{3o}.$$

Here $\mathbf{k}_i$ are the wave vectors of pumping ($i = 1$ and 2) and laser ($i = 3$) radiation. The first two relations describe the generation of direct FIR waves, while the other two are for the backward ones.
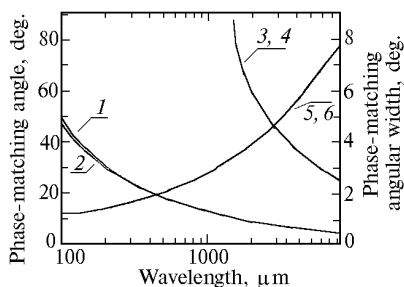

Fig. 2. Phase-matching curves for CO_2 laser difference frequency generation for the following interactions: å–î→å (*1*) and å–î→î (*2*) direct interactions, î–å→î (*3*) and î–å→å (*4*) backward ones; spectral dependences of phase-matching angular widths for å–î→å and î–å→î (*5, 6*) interactions.

The ZnGeP$_2$ crystal considered in this work has a $\overline{4}2m$ point symmetry group and a coefficient of quadratic nonlinear susceptibility, $d_{14} = d_{36} = 7.5 \cdot 10^{-11}$ m/V,

which is the third in magnitude among all crystals known. Since there is a fundamental crystal absorption band between pumping and generated waves for the three-frequency interaction under investigation, the Kleinman conditions are violated. In this case the coefficients of quadratic nonlinear susceptibility are the following: $d_{eff} = -d_{36} \sin \theta \sin 2\varphi$ and $d_{eff} = (d_{14} + d_{36}) \sin\theta \cos\theta \times \cos 2\varphi = d_{14} \sin2\theta \cos2\varphi$ for the first two interaction types, and $d_{eff} = d_{14} \sin2\theta \cos2\varphi$ and $d_{eff} = -d_{14} \times \sin\theta \sin2\varphi$ for the backward wave generation. Here θ is the angle between the optical axis and the pumping wave vectors, φ is the angle between the **XZ** crystallographic plane and **kZ** plane.

In the plane-wave approximation and a preset pumping field, the following relation has been used to estimate the power conversion efficiency:

$$\eta = \frac{P_3}{\sqrt{P_1 P_2}} = \frac{4\pi d_{eff}^2}{\varepsilon_0 cn_1 n_2 n_3} \frac{\sqrt{P_1 P_2}}{(r_1^2 + r_2^2)} \frac{L^2}{\lambda_3^2} \times$$
$$\times \sin c^2 (\Delta kL / 2) T_1 T_2 T_3 K,$$

where $Ð_1$, and $Ð_2$ are the pumping powers; r_1 and r_2 are the efficient pumping beam radii at the half maximum level; L is the crystal length; Δk is the phase mismatch for the interacting waves; $T_i = 4n_i/(n_i + 1)^2$ is the transmission of the input and output crystal edges at normal light incidence (with the account of Fresnel losses);

$$K = e^{-\alpha_3 L} \frac{1 + e^{-\Delta\alpha L} - 2e^{(-\Delta\alpha L)/2} \cos (\Delta kL)}{(\Delta kL + 0.5 \Delta\alpha L)},$$

where $\Delta\alpha = \alpha_1 + \alpha_2 - \alpha_3$. To exclude the walk-off effect and increase a conversion efficiency, the condition $r_1 = r_2 > L\rho/\pi$ should hold for r_1 and r_2 beams, where ρ is a birefringence angle. Since the angular phase-matching widths are of the order of degrees and exceed the phase-matching angle difference, both ordinary and extraordinary FIR waves should be generated simultaneously. This is true for both interaction pairs. As pumping decreases weakly, this effect increases the total conversion efficiency.

When using sub-nanosecond and mode-locked lasers, the conversion efficiency of 2.5% is achievable (pumping power density is 10^9 W/cm^2). However, as known, a decrease in pulse duration results in an increase in the emission line width, so it is impossible to keep the line width within 10^{-3} cm^{-1}.

The efficiency may reach up to 0.1 and $5 \cdot 10^{-4}$% for TEA and cw lasers, respectively (pumping power density is $5 \cdot 10^7$ and $2 \cdot 10^5$ W/cm^2).

Further increase in efficiency is limited by a thermal lens formation that can damage the crystal surface. The estimations were made for short-wavelength portions of the submillimeter spectral range. When the difference wavelength generated becomes comparable with the pumping beam radii r_1 and r_2, diffraction effects amplify and the plane-wave approximation does not work.

Applicability of the FIR source considered to analysis of gas mixture composition is illustrated in Fig. 3. This figure presents the spectral behaviors of absorption coefficients for some gases; these results were obtained with the use of HITRAN–96 atlas. Table 2, which is only illustration, presents some coincidence of CO_2 laser difference frequencies and intense gas absorption lines.

Table 2. Coincidence of converted CO_2 laser emission lines with the absorption lines of some gases.

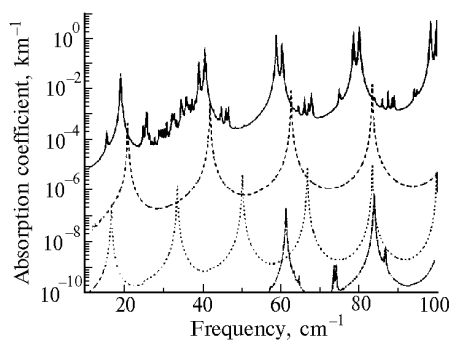| Combination of CO_2 laser lines	FIR frequency v, cm^{-1}	Absorption line center, v, cm^{-1}	Δv, cm^{-1}	Line intensity, $\dfrac{cm}{molecule} \cdot 10^{20}$	Gas
$9P(2)–9P(46)$	41.109	41.111	0.002	98.80	HF
$9R(32)–9P(44)$	62.576	62.584	0.008	24.92	HCl
$9R(50)–9P(32)$	59.313	59.312	0.001	1.72	HOCl
$9P(18)–9R(4)$	83.892	83.869	0.023	76.1	OH
$9P(40)–10P(38)$	98.365	98.348	0.015	44.7	NH_3
$9R(8)–10R(12)$	99.915	99.915	0.000	12.10	HBr

Fig. 3. Spectral dependence of the absorption coefficients for NH_3 (solid curve), HCl (dotted curve), HBr (dashed curve), and OH (dash-and-dot curve) at 1 ppm concentration.

When developing real spectral instrumentation and gas analyzers, one should take into account strong H_2O vapor and O_2 interference. This interference decreases significantly when passing to SH frequency region.

The summing of CO_2 laser radiation and SHF radiation with $ZnGeP_2$ crystals also seems to be interesting because it gives a chance for precision frequency detuning from strictly fixed CO_2 laser emission lines and working in the frequency sweeping mode. The operation of the difference frequency converter confirms the feasibility of such a conversion.

Thus, the Sellmeier equations for the FIR spectral range have been determined based on integrated data on the optical properties of $ZnGeP_2$ crystals. These equations gave the grounds for predicting the possibility of CO_2 laser emission conversion into the FIR spectral range when phase-matching conditions are realized for four interaction types. This allows one to increase the conversion efficiency up to units of percent.

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