Generation of mid-infrared pulses by $\chi^{(3)}$ difference frequency generation in CaF$_2$ and BaF$_2$

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Tunable mid-IR pulses in the range 1300–4200 cm$^{-1}$ (7.7–2.4 $\mu$m) are generated through a phase-matched four-wave mixing process in ordinary mid-IR window materials such as CaF$_2$ and BaF$_2$. In this process the difference frequency $\nu_3 = 2\nu_2 - \nu_1$ is generated from pump fields $\nu_1$ and $\nu_2$. The process can be phase matched to different frequencies by adjustment of the angle between the pump fields.© 2001 Optical Society of America

Mid-IR spectroscopy, which covers roughly the wavelength range 2.5–10 $\mu$m, has a long tradition as an analytical tool in chemistry, since molecular vibrations typically absorb in this wavelength range. However, linear mid-IR spectroscopy provides no information on processes on short time scales. The study of these processes requires time-resolved (or nonlinear) mid-IR spectroscopic techniques that employ high-intensity picosecond or femtosecond pulses. For example, in studies of the O–H stretch vibration in water$^{1,2}$ and the C–O vibration in organic molecules,$^{3,4}$ most dynamics (energy relaxation, molecular reorientation) occurs on a typical time scale of 1 ps.

The common methods for generating femtosecond mid-IR pulses employ various kinds of three-wave mixing processes, such as difference frequency generation$^5$ and optical parametric generation and (or) amplification (OPG/OPA).$^7$–$^9$ Reference 10 is a review of several OPG/OPA methods. These processes all rely on the second-order polarization $P^{(2)}(t) \propto \chi^{(2)} E^2(t)$ created by a high-intensity field $E(t)$. This second-order polarization is nonzero only in materials that lack inversion symmetry. In such a system, fields with frequencies $\nu_1$ and $\nu_2$ couple to a field with frequency $\nu_3 = \nu_1 \pm \nu_2$. A high efficiency can be obtained only if the phase-matching condition $k_x = k_1 \pm k_2$ is fulfilled. The wave vectors $k_x$ have magnitudes $k_x = \nu_x/n_x$, where $n_x$ is the index of refraction at frequency $\nu_x$ (we use the wave number [in cm$^{-1}$] as a frequency quantity). Since in a medium with a normal dispersion, $n(\nu)$ is a monotonically increasing function of $\nu$, the phase-matching condition can be satisfied only if the different fields have different polarizations, and the birefringence of the $\chi^{(2)}$ material is used, such that the $\nu_3$ field experiences a lower index of refraction than the $\nu_2$ field. Hence, to be suitable for $\chi^{(2)}$ IR generation a crystal should (1) be transparent for the wavelengths involved, (2) lack inversion symmetry, and (3) have the right amount of birefringence. Unfortunately, the available crystals for wavelengths beyond 4.5 $\mu$m, such as AgGaS$_2$, GaSe, and ZnGeP$_2$, cannot be directly pumped with the currently available high-intensity 800-nm Ti:sapphire lasers.

As an alternative to the $\chi^{(2)}$-based pulse generation discussed above, we now consider $\chi^{(3)}$ (or four-wave mixing) processes. Here, three fields interact and drive a third-order polarization $P^{(3)}(t) \propto \chi^{(3)} E^3(t)$. Compared with $\chi^{(2)}$ processes, $\chi^{(3)}$ processes have the advantage that $\chi^{(3)}$ is nonzero in any medium, without any restrictions on the crystal symmetry. Therefore, $\chi^{(3)}$ frequency mixing is, in principle, possible in any medium, including isotropic media. Since such media have no birefringence, one must use alternative means to fulfill the requirement of phase matching.

Thus, pulses in various wavelength ranges have been generated. For example, far-IR ($\sim 60$-cm$^{-1}$) pulses have been generated in air.$^{11}$ Because of the low value of $\chi^{(3)}$ in air, the pulse energy was only $\sim 5$ pJ, which required time-gated and phase-sensitive terahertz detection schemes. In the UV the properties of certain modes in hollow fibers have been employed to generate light in gases at well-chosen pressures with $\sim 4$-$\mu$J pulse energies.$^{13}$ Further, in the mid IR, 1064-nm and tunable dye-laser pulses have been combined for generation of tunable picosecond pulses.
pulses at \( \sim 1\text{-pJ} \) pulse energies in a phase-matched \( \chi^{(3)} \) process.\textsuperscript{14}

In this Letter we show how the approach reported in Ref. 14 can be used to generate mid-IR (2.4–7.6-\( \mu \)m) pulses with high energies and femtosecond durations with the currently available titanium sapphire laser systems. Here, pump fields with frequencies \( \tilde{\nu}_1 \) and \( \tilde{\nu}_2 \) generate a difference frequency \( \tilde{\nu}_3 = 2\tilde{\nu}_2 - \tilde{\nu}_1 \), with \( \mathbf{k}_3 = 2\mathbf{k}_2 - \mathbf{k}_1 \) as the phase-matching condition. We use the common window materials CaF\(_2\) and BaF\(_2\) as generating media. In these nonbirefringent materials, phase matching is possible, despite the fact that they have a normal dispersion, because this process uses the high-frequency field \( 2\tilde{\nu}_2 \), with an index of refraction \( n(\tilde{\nu}_3) < n(\tilde{\nu}_1) \).

For a pump frequency \( \tilde{\nu}_1 = 12400 \text{ cm}^{-1} \) (806 nm), it turns out that collinear phase matching occurs at \( \tilde{\nu}_3 = 2540 \text{ cm}^{-1} \) (3.9 \( \mu \)m) in CaF\(_2\). Similarly, 7.8-\( \mu \)m light can be generated in BaF\(_2\). Since these materials are not birefringent, rotating the crystal does not affect the wavelength at which the process is phase matched. However, the phase-matching can be tuned with the angle between the pump beams.

We used a commercial Ti:sapphire laser (Quantinix Titan; 100-fs, 2.5-mJ pulses, 1-kHz repetition rate) to pump a \( \beta \)-barium borate optical parametric conversion stage (Light Conversion Topas). From the output of the parametric conversion stage, we used the signal (6250–8300 cm\(^{-1}\), 300 \( \mu \)J) and the remaining pump (12400 cm\(^{-1}\), 1.1 mJ) for the \( \tilde{\nu}_2 \) and \( \tilde{\nu}_1 \) fields, respectively, as shown in Fig. 1. After being split and recombined for time overlap, the pulses were collimated to an approximately 2-mm diameter before interacting in a 4-mm CaF\(_2\) or BaF\(_2\) plate. Because of the properties of the \( \chi^{(3)} \) tensor, the intensity of the generated \( \tilde{\nu}_3 \) field is a factor of 9 higher for parallel \( \tilde{\nu}_1 \) and \( \tilde{\nu}_2 \) pump fields than for perpendicular pump fields.\textsuperscript{15} Therefore, we used a wave plate to make the polarizations of the pump and signal pulses parallel.

A delay stage permitted adjustment of the time overlap between the pump and signal pulses. At time overlap, we generated pulses with typical energies of 100–200 nJ.

If the laser pulses are focused in air in a collinear geometry, similar to Ref. 12, a measurable amount of IR is generated as well with a typical energy of only 3 nJ and a bandwidth of 400 cm\(^{-1}\) FWHM. Also, a visible amount of light at frequency \( 2\tilde{\nu}_1 - \tilde{\nu}_2 \) is generated in this case.

Figure 2 shows the tuning curve with the generated frequency, \( \tilde{\nu}_3 \), versus the angle \( \beta = \angle \mathbf{k}_1, \mathbf{k}_3 \). Calculated tuning curves are shown as well; we obtain these by substituting \( k_3 = n_3 \tilde{\nu}_3 \) in the phase-matching condition \( \mathbf{k}_3 = 2\mathbf{k}_2 - \mathbf{k}_1 \), which yields

\[
\cos(\beta) = \frac{4n_2^2\tilde{\nu}_2^2 - n_1^2\tilde{\nu}_1^2 - n_3^2\tilde{\nu}_3^2}{2n_1n_3\tilde{\nu}_1\tilde{\nu}_3},
\]

where \( n_i \) are the indices of refraction as calculated from the Sellmeier equations for CaF\(_2\) (Refs. 16 and 17) and BaF\(_2\).\textsuperscript{16,18}

For BaF\(_2\), we obtained better agreement between the experiment and the calculated tuning curve if we increased the index of refraction at frequency \( \tilde{\nu}_3 \) by \( 1.0 \times 10^{-4} \). Instead of 1286 cm\(^{-1}\) (7.8 \( \mu \)m) and 6.5\(^\circ\) for the cutoff frequency and maximum angle, respectively, \( n_3 \) yields 1325 cm\(^{-1}\) and 6.0\(^\circ\), respectively (as shown in Fig. 2). In CaF\(_2\), the difference between experiment and theory can result from a frequency-dependent deviation of less than \( 10^{-4} \) in the refractive index for the \( \tilde{\nu}_2 \) field. We note that the experimental values of the index of refraction are known to differ by similar amounts from the calculated values.\textsuperscript{16–18}

Figure 3 shows typical spectra of the pulses generated in CaF\(_2\) and BaF\(_2\). We obtained these spectra with a scanning monochromator and PbSe (for the CaF\(_2\) data) and HgCdTe (for BaF\(_2\)) detectors. We chose these detectors for their different spectral responses. To tune \( \tilde{\nu}_3 \), we adjusted both \( \tilde{\nu}_2 \) (which defines the difference frequency \( \tilde{\nu}_3 \)) and the angle between \( \mathbf{k}_1 \) and \( \mathbf{k}_3 \) (phase matching). The FWHM bandwidth of the generated spectra is \( \sim 200 \text{ cm}^{-1} \) for CaF\(_2\) and 40–300 cm\(^{-1}\) for BaF\(_2\), respectively. The maximum frequency \( \tilde{\nu}_3 \) is approximately 4100 cm\(^{-1}\), limited by \( \tilde{\nu}_2 \), which could not be tuned higher than \( \sim 8250 \text{ cm}^{-1} \) in our OPG/OPA.
Fig. 3. Typical spectra of the generated pulses in CaF$_2$ and BaF$_2$. The structure in the spectra at 1500 and 3700 cm$^{-1}$ is caused by absorption lines of water vapor.

Fig. 4. Autocorrelate of pulses generated in CaF$_2$ at 2580 cm$^{-1}$ with a fit to a Gaussian pulse shape. SFG, sum frequency generation.

Figure 4 shows an autocorrelate for pulses generated in CaF$_2$ at 2580 cm$^{-1}$. We measured this by generating the second harmonic of the IR pulses in a LiIO$_4$ crystal. The FWHM autocorrelate width is 298 fs, which corresponds to a 211-fs pulses duration if we assume a Gaussian pulse shape. With a 200-cm$^{-1}$ FWHM bandwidth, this yields $\Delta \nu \Delta \tau = 1.3$ for the frequency–bandwidth product.

To summarize, we have shown that a $\chi^{(3)}$ difference frequency generation process with two pump fields can be phase matched in the common IR window materials CaF$_2$ and BaF$_2$, which have no special birefringent or crystal symmetry properties. An 806-nm laser pulse as the high-frequency ($\tilde{\nu}_2$) pump permits generation of difference frequencies over the range 2.4–7.6 $\mu$m with the angle between the pumping fields as a tuning parameter. We obtained pulse energies of up to 200 nJ.

As a final note we point out that the presented type of $\chi^{(3)}$ difference frequency generation can be phase matched in any material with a normal dispersion relation, although the angles and cutoff wavelengths vary. A common material especially worth mentioning in this respect is NaCl, with $\tilde{\nu}_3 > 600$ cm$^{-1}$ and $\beta < 17^\circ$.

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References