Higher-order nonlinear processes in $CdGeAs_2$

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Phase-matched fourth-harmonic generation in $CdGeAs_2$ is reported. The measured effective fourth-order nonlinear coefficient is $\chi^{(4)}_{I,\mathrm{eff}}/\epsilon_0 = 8\times10^{-27}$ m^3/V^3. The contribution of cascade processes, connected with lower-order nonlinearities, to the effective third- and fourth-order nonlinear coefficients is discussed.

We report observation of phase-matched fourth-harmonic generation (FHG) in $CdGeAs_2$ using a CO_2 pump laser with a 140-nsec pulse duration. From the measurements we determine an effective fourth-order susceptibility tensor which is much higher than previous theoretical estimates.[1,2]

Measurements of higher-order nonlinearities are complicated because of interference between the direct processes and cascade processes connected with lower-order nonlinearities. The susceptibility tensors obtained by these measurements are effective values that include the contributions of the cascade processes. For $CdGeAs_2$ the estimated contributions of these processes to the effective third- and fourth-order susceptibility tensors are comparable to the measured values.

Quantitative studies of higher-order nonlinear optical processes are important for the understanding of the nonlinear properties of dielectric media. Ninth-harmonic generation has recently been reported[3] in a gaseous sodium-argon mixture and phase-matched fourth- and fifth-harmonic generation in solids have been observed in lithium formate[4] and calcite,[5] respectively. These experiments were conducted in the visible and ultraviolet spectral regions with picosecond pump pulses from a model-locked Nd^{3+} glass laser. The present experiment is the first measurement of an effective fourth-order susceptibility tensor for an infrared material.

The interest in $CdGeAs_2$ during recent years derives from its large second-order nonlinear coefficient. The material is useful for frequency doubling of CO_2 laser radiation, and energy conversion efficiencies as high as 27% have been reported.[6] Both its second-order[7,8] and effective third-order[9] nonlinear coefficients have been measured. Because it has the chalcopyrite structure ($42m$ symmetry), $CdGeAs_2$ has only two independent fourth-order nonlinear coefficients, $\chi^{(4)}_{xyzzz}$ and $\chi^{(4)}_{xyyyz} = \chi^{(4)}_{xxxyz}$.[10]

$CdGeAs_2$ is one of the few infrared nonlinear materials with sufficient birefringence to allow phase-matched FHG. Type-I phase matching is satisfied at pump wavelengths longer than 9.7 μm, and type-II phase matching is allowed at wavelengths between 12.4 and 15.2 μm.[1,8] The type-I phase matching condition can be stated as

$$n_4^o = n_1^e(\theta), \tag{1}$$

where o and e refer to ordinary and extraordinary waves, respectively, and θ is the angle between the wave vector and the optical axis (z axis). If φ is the azimuth angle between the x axis and the projection of the wave vector in the x-y plane,[11] the fourth-order nonlinear coefficient for type-I phase matching can be written

$$\chi_I^{(4)}(\omega,\omega,\omega,\omega) = 2\sin2\theta\cos2\varphi(\chi^{(4)}_{xyzzz}\sin^2\theta + \chi^{(4)}_{xyyyz}\cos^2\theta). \tag{2}$$

This expression is maximized for an input wave polarized either in the x-z or y-z plane ($\varphi = 0$ or $\frac{1}{2}\pi$, respectively).

A direct measurement of $\chi_I^{(4)}(\omega,\omega,\omega,\omega)$ is not possible because of interference between the direct FHG process and the two- and three-step cascade processes involving the lower-order nonlinearities $\chi^{(2)}$ and $\chi^{(3)}$. The cascade processes are automatically phase matched in the same direction [defined by Eq. (1)] as the direct process even though the individual cascade steps are generally not phase matched in the same direction.[12] The effective nonlinearity which is measured can therefore be written[2]

$$\begin{aligned}\chi^{(4)}_{1,\mathrm{eff}}(4\omega) = {}& \chi_I^{(4)}(\omega,\omega,\omega,\omega) + b_1\chi^{(2)}(\omega,\omega)\\ &\times\chi^{(3)}(2\omega,\omega,\omega) + b_2\chi^{(3)}(\omega,\omega,\omega)\chi^{(2)}(3\omega,\omega)\\ &+ b_3\chi^{(2)}(\omega,\omega)\chi^{(2)}(2\omega,\omega)\chi^{(2)}(3\omega,\omega)\\ &+ b_4[\chi^{(2)}(\omega,\omega)]^2\chi^{(2)}(2\omega,2\omega).\end{aligned} \tag{3}$$

The last term vanishes in the type-I phase-matching geometry that maximizes $\chi_I^{(4)}(\omega,\omega,\omega,\omega)$. In this case ($\varphi = \frac{1}{2}\pi$), Eq. (3) takes the specific form

$$\chi^{(4)}_{1,\mathrm{eff}}(4\omega) = -2\sin 2\theta\left(\chi^{(4)}_{xyzzz}\sin^2\theta + \chi^{(4)}_{xyyyz}\cos^2\theta + \frac{3\chi^{(2)}_{xyz}}{4n_2^o[n_1^e(\theta)-n_2^o]\epsilon_0}\left(\chi^{(3)}_{xxzz}\sin^2\theta + \chi^{(3)}_{xxyy}\cos^2\theta\right)\right.$$
$$+ \frac{\chi^{(2)}_{xyz}}{2n_3^e(\theta)[n_1^e(\theta)-n_3^e(\theta)]\epsilon_0}\left(\chi^{(3)}_{zzzz}\sin^4\theta + \chi^{(3)}_{xxxx}\cos^4\theta + 6\chi^{(3)}_{xxzz}\sin^2\theta\cos^2\theta\right)$$
$$\left. + \frac{(\chi^{(2)}_{xyz})^3\sin^2 2\theta}{2n_3^e(\theta)n_2^o[n_1^e(\theta)-n_2^o][n_1^e(\theta)-n_3^e(\theta)]\epsilon_0^2}\right). \tag{4}$$

This equation is valid as long as the coherence lengths associated with the intermediate steps of the cascade processes are shorter than both the crystal length and the absorption length.

The cascade processes can result in significant fourth-harmonic power in directions other than the one defined by Eq. (1) when one of the individual steps is phase matched, even though the overall process is not phase matched in this case. For example, the final steps of the cascade processes associated with the b_1 and b_3 terms in Eq. (3) [or equivalently the second and fourth terms in Eq. (4)] are phase matched when $n_1^e(\theta)+n_2^o=2n_4^o$, and the b_2 and b_3 terms [or third and fourth terms in Eq. (4)] are phase matched for $n_1^e(\theta)+3n_3^e(\theta)=4n_4^o$. In $CdGeAs_2$ only the latter phase-matching condition is satisfied ($\theta=40.1°$ at $\lambda_1=10.6\ \mu$m). The form of the b_3 term is modified under these new phase-matching conditions while the b_1 and b_2 terms remain the same as for the case of overall phase matching. The first or intermediate steps of the cascade processes may also be phase matched. The interference terms, however, then change. The b_1 and b_2 terms are phase matched when $n_1^e(\theta)=n_2^o$ and $n_1^e(\theta)=n_3^e(\theta)$, respectively, whereas the b_3 term is phase matched both under these conditions and also when $n_1^e(\theta)+2n_2^o=3n_3^e(\theta)$. In $CdGeAs_2$ only the condition $n_1^e(\theta)=n_2^o$ is satisfied ($\theta=33.4°$ at $\lambda_1=10.6\ \mu$m).

The fourth-harmonic component of the macroscopic polarization generated by an applied electric field $\mathcal{E}_1$ is given by $\mathcal{P}_4=\chi^{(4)}_{1,\mathrm{eff}}\mathcal{E}_1^4$, where $\mathcal{P}_4$ and $\mathcal{E}_1$ are defined as the Fourier amplitudes of the fields. The resulting fourth-harmonic power P_4 generated in a crystal of length d, assuming weak focusing and a TEM_{00} mode pump, is given by

$$P_4 = 128\eta_0^5\left(\frac{\omega_1\chi^{(4)}_{1,\mathrm{eff}}}{[n_1^e(\theta)+1]^4(n_4^o+1)}\right)^2 \times \frac{P_1^4}{A_1^3}\,\frac{\sin^2(\Delta kd/2)+\sinh^2(ad/4)}{(\Delta k/2)^2+(a/4)^2} \times \exp[-(a_4/2+2a_1)d], \tag{5}$$

where $\eta_0=377\ \Omega$ is the free-space impedance, P_1 is the incident pump power, $A_1=\frac{1}{2}\pi w_1^2$ is the beam area expressed by the spot size w_1, $\Delta k=k_4^o-4k_1^e$ is the wave-vector mismatch, a_4 and a_1 are the respective intensity attentuation coefficients at the fourth-harmonic and fundamental frequencies, and $a=a_4-4a_1$. Equation (5) corrects for the reflection losses at the crystal entrance and exit face.

A grating-tuned, TEM_{00} mode, CO_2 TEA laser was used in the experiments. The laser had a low-pressure, longitudinally pulsed gain cell inside the cavity.[13] This ensured single-longitudinal-mode operation during the $\chi^{(4)}_{1,\mathrm{eff}}$ measurements. The laser energy was measured with a Gen-Tec ED-200 joulemeter, and the pulse duration of 140 nsec was monitored by a photon drag detector. The laser beam was passed through an 8-μm-long-wavelength pass filter to block the 4.3-μm fluorescence from the laser tube and the third-harmonic signal generated in the germanium output mirror of the laser before being focused by a 2.2-m radius mirror into the $CdGeAs_2$ crystal. The crystal had been oriented and cut for optimum FHG ($\varphi=\frac{1}{2}\pi$) and was mounted in a Dewar equipped with a BaF_2 entrance window and a 5-mm LiF exit window. The crystal was kept at liquid-nitrogen temperature in order to reduce absorption losses.[6] The focused spot size was 480 μm, as determined from the measured transmission through several calibrated apertures. The output from the Dewar was passed through a 6.4-mm quartz window and a 2.1- to 2.7-μm band-pass filter before being detected by an InSb photovoltaic detector. Two different detectors were used with time constants of, respectively, 0.53 and 1.8 μsec. The detectors did not resolve the fourth-harmonic pulse and this necessitated a correction before determining conversion efficiencies. The detector reponsivities were determined from measurements at 3.39 μm using a He-Ne laser of known output power and assuming that the quantum efficiency was the same at the fourth-harmonic wavelengths.

Two $CdGeAs_2$ crystals 2.7 mm and 3.8 mm long, referred to as A and B, were used in the experiments. Their measured absorption constants at liquid-nitrogen temperature at 10.25 μm and 2.56 μm were, respectively, $a_1=0.1\ \mathrm{cm}^{-1}$ and $a_4=4.4\ \mathrm{cm}^{-1}$ for crystal A and $a_1=1.9\ \mathrm{cm}^{-1}$ and $a_4=9.5\ \mathrm{cm}^{-1}$ for crystal B. Both crystals were cut for type-I phase matching. The measured polarization

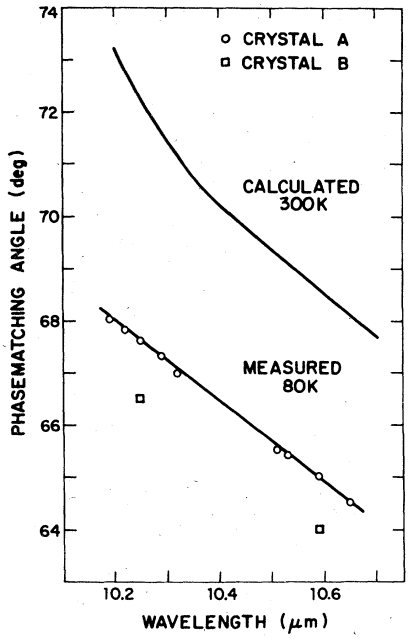

FIG. 1. Type-I phase-matching angle for FHG in $CdGeAs_2$.

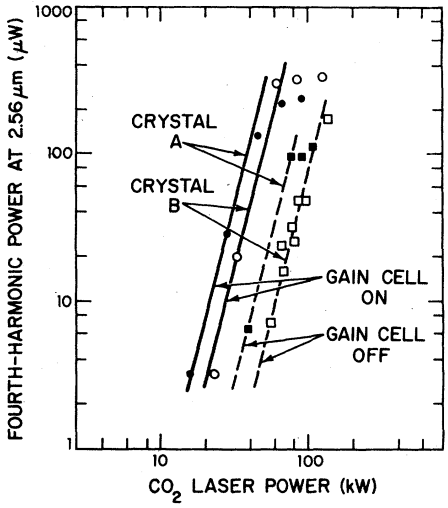

FIG. 2. Input-output curve for FHG in $CdGeAs_2$ ($w_1 = 480\ \mu m$, $d_A = 0.27$ cm, and $d_B = 0.38$ cm).

of the fourth-harmonic output beam was perpendicular to the input beam polarization, as expected for type-I phase matching. Figure 1 shows the measured wavelength dependence of the type-I phase-matching angle for FHG. The measured angles have an absolute uncertainty of ±1°. The figure also shows a phase-matching curve calculated from refractive-index data[8] taken at room temperature. Previously we have shown that the phase-matching angle for second-harmonic generation (SHG) of CO_2 laser radiation is only weakly temperature dependent, varying by less than 1°K between room temperature and liquid-nitrogen temperature.[6] A stronger temperature dependence is expected for FHG since the fourth-harmonic wavelength is close to the wavelength corresponding to the $CdGeAs_2$ bandgap, which varies from 2.2 μm at room temperature to 1.9 μm at liquid-nitrogen temperature.[14] The increased band gap at liquid-nitrogen temperature should reduce the indices of refraction at the fourth-harmonic wavelength and consequently lead to a smaller phase-matching angle. In Fig. 1 this effect is particularly evident at the shortest pump wavelengths where the measured phase-matching angle is ~5° smaller than calculated. At 10.6 μm the difference is 3.5°, which is slightly larger than the difference of 2° for the phase-matching angle of SHG with 10.6-μm radiation.

The θ dependence of the fourth-harmonic output power when the crystals were rotated through their phase-matching positions agreed with Eq. (5). The measured external angular width (FWHM) for crystal A at $\lambda_1 = 10.6$ μm was $\Delta\theta_{ext} = 2.6°$, in good agreement with the calculated angle of $\Delta\theta_{ext} = 40\lambda_1/\pi d \tan\rho = 3.0°$ for negligible absorption and a walk-off angle $\rho = 0.96°$.

The measured fourth-harmonic output power at 2.56 μm versus input power at 10.24 μm for the two crystals with the gain cell on and off is shown in Fig. 2. Turning the gain cell off resulted in partial mode locking of the laser pulse, increasing the conversion efficiency by 15 to 20 times. For the mode-locked case, Fig. 2 gives the average peak power. The conversion efficiency saturates at power levels approaching the laser-induced surface damage threshold. The saturation is less evident when the gain cell is on. This suggests an intensity dependent effect. From the measured input-output curves in the case of no mode locking, together with Eq. (5), we determine the effective fourth-order susceptibility tensor $\chi^{(4)}_{1,\mathrm{eff}}$, in mks units, as 6.2×10^{-38} and 8.0×10^{-38} for crystals A and B, respectively. In order to reduce the possibility of systematic errors, $\chi^{(4)}_{1,\mathrm{eff}}$ for crystal A was also measured in another setup using a different laser and detector. The results of the two measurements agreed within 20%. From the experiments on both crystals we obtain

$$\chi^{(4)}_{1,\mathrm{eff}} = 7\times10^{-38}\ \frac{\mathrm{m^2\,A\,sec}}{\mathrm{V^4}} \pm 40\%$$

for $CdGeAs_2$.

The intrinsic breakdown thresholds in solids are determined by electron avalanche ionization,[15] which occurs at electric field strengths of typically 10^8 V/m. To reach this intrinsic threshold in $CdGeAs_2$ probably requires CO_2 laser pulses short-

TABLE I. Measured linear and nonlinear susceptibilities of $CdGeAs_2$.

$\chi^{(1)}_{zz}/\epsilon_0$	$=12$ [a]
$\chi^{(2)}_{xyz}/\epsilon_0$	$= 6.1\times10^{-10}$ m/V [b]
$\chi^{(3)}_{II,eff}/\epsilon_0$	$= 7.0\times10^{-18}$ m^2/V^2 [c]
$\chi^{(4)}_{I,eff}/\epsilon_0$	$= 7.9\times10^{-27}$ m^3/V^3 [d]

[a] References 7 and 8.
[b] References 7 and 16.
[c] References 1 and 9.
[d] This work.

er than 1 nsec. In Table I the measured $\chi^{(4)}_{I,eff}/\epsilon_0$ is compared with the lower-order nonlinear susceptibilities. The higher-order terms in the expansion of the induced polarization do not exceed the lower-order terms even at the threshold for dielectric breakdown.

The $\chi^{(3)}_{eff}$ value in Table I was measured[1,9] for type-II phase matching. The value seems high when compared to the general trend in $\chi^{(n)}$. The large value has been attributed to the free-carrier contribution due to the nonparabolicity of the energy bands.[9] According to Ref. 1, however, the measured $\chi^{(3)}_{eff}$ is more than 20 times the theoretical value that includes both the free-carrier and bound-electron contributions to $\chi^{(3)}_{eff}$. This discrepancy can be attributed to cascade processes, which were not discussed in Refs. 1 and 9. These give rise to interference terms proportional to $\chi^{(2)}(\omega,\omega)\chi^{(2)}(2\omega,\omega)$. The calculated contribution to $\chi^{(3)}_{eff}/\epsilon_0$ due to the cascade processes is

$$\left(\frac{\chi^{(2)}_{xyz}\sin\theta}{\epsilon_0}\right)^2 \times\left(\frac{3\cos^2\theta}{n_2^e(\theta)[n_1^e(\theta)-n_2^e(\theta)]}-\frac{1}{n_2^o[n_1^e(\theta)-n_2^o]}\right)\cos\theta$$

for type-I phase matching, and

$$\frac{4}{\sqrt{3}}\left(\frac{\chi^{(2)}_{xyz}\sin\theta}{\epsilon_0}\right)^2 \times\left(\frac{2}{3n_2^o[n_1^e(\theta)+n_1^o-2n_2^o]}-\frac{\cos^2\theta}{2n_2^e(\theta)[n_1^e(\theta)-n_2^e(\theta)]}\right)$$

for type-II phase matching. Inserting numerical values gives -3.7×10^{-18} and 7.7×10^{-18} m^2/V^2, respectively. The latter result is comparable with the measured $\chi^{(3)}_{II,eff}/\epsilon_0$ of 7.0×10^{-18} m^2/V^2.

The interference terms for the fourth-order process can only be estimated, since the sign and magnitude of each $\chi^{(3)}_{iijj}$ component are not known. An upper bound can be determined using the reported $\chi^{(3)}_{eff}$ value for type-II phase matching, keeping in mind that this value most likely is greater than the $\chi^{(3)}_{iijj}$ components because of the interference effects. The estimated contribution to $\chi^{(4)}_{I,eff}/\epsilon_0$ in Eq. (4) due to the cascade terms is 1.7×10^{-26} m^3/V^3 assuming $\chi^{(3)}_{iijj}\approx\chi^{(3)}_{iiii}/3\approx\chi^{(3)}_{eff}>0$. This is of the same order of magnitude as the measured value of $\chi^{(4)}_{I,eff}/\epsilon_0$.

The $\chi^{(4)}_I(\omega,\omega,\omega,\omega)/\epsilon_0$ for $CdGeAs_2$ has been theoretically estimated as 1.3×10^{-29} m^3/V^3 using a bond-orbital model[1] and as 0.7×10^{-29} m^3/V^3 from a simple anharmonic-oscillator model.[2] These estimates are smaller than the measured $\chi^{(4)}_{I,eff}/\epsilon_0$ value by factors of almost 10^3. This suggest that the interference terms make the main contribution to $\chi^{(4)}_{I,eff}$. The theory may be in error, however, since theory and experiment differ by a factor of 50 for lithium formate,[2] the only other material for which fourth-order nonlinear processes have been studied.

In summary, we have observed phase-matched FHG in $CdGeAs_2$ and have determined its effective fourth-order nonlinear coefficient. The measured $\chi^{(4)}_{I,eff}$ is three orders of magnitude larger than the theoretical estimates for $\chi^{(4)}_I(\omega,\omega,\omega,\omega)$. The importance of cascade processes has been examined. These may contribute significantly to $\chi^{(4)}_{I,eff}$. Similarly we have found that interference terms also are important for the interpretation of the $\chi^{(3)}_{II,eff}$ measurement for $CdGeAs_2$ reported in the literature.

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