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OPTICAL HARMONIC GENERATION IN THE INFRARED USING A CO_2 LASER

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Recently, second-harmonic generation (SHG) in tellurium was reported[1] using a CO_2 laser at 10.6 μ under phase-matched conditions. In this paper we report optical harmonic generation in the infrared (with a CO_2 laser) in (a) zinc blende crystals ($\bar{4}3m$) InAs, GaAs, ZnS, CdTe, ZnSe, and ZnTe; (b) hexagonal crystals ($6mm$) ZnS, CdS, and CdSe; and (c) a trigonal crystal (32), Se. (SHG in some of these crystals has been previously reported in reflection[2] and transmission[3] experiments using ruby laser at 6943 Å and neodymium laser at 1.06 μ.) Using an unfocused CO_2 laser in cw[4] and Q-switched[5] operation, we have obtained the nonlinear coefficients for these materials at 10.6 μ. Phase matching was achieved in single-crystal selenium at $\theta_m \approx 10°$ from the optic axis. Since the band gap of selenium is at ~8000 Å, the large nonlinear coefficient $d_{11}(\mathrm{Se}) = 1.9 \times 10^{-7}$ esu should allow the use of Se as a phase-matchable nonlinear optical material at wavelengths shorter than those possible in tellurium.[1] Even in the materials where phase matching was not possible (because of lack of birefringence), sizable SHG could be obtained due to long coherence lengths. These arise because of the rather small dispersion between 5.3 and 10.6 μ in most of the materials investigated here, particularly in ZnTe and CdTe. In addition, coherence-length measurements reported in this paper provide refractive-index dispersion $(n_{5.3\,\mu}-n_{10.6\,\mu})$ for a number of materials where no such measurements exist.

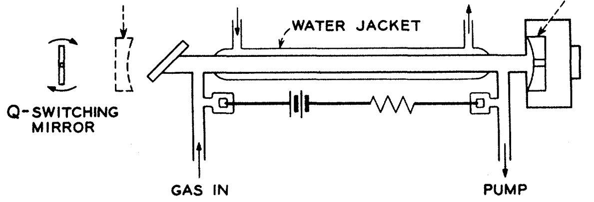

FIG. 1. Experimental set-up used for cw and Q-switched optical harmonic-generation experiments.

The CO_2 laser used in these experiments is shown schematically in Fig. 1. The laser tube was 25 mm i.d. and 2 m long. (For details of the CO_2 laser, see Ref. 4.) The Q-switching mirror was gold coated and was rotated at speeds up to 120 rps using a synchronous motor. For cw operation the concave mirror M_2 was inserted. Energy was coupled out from mirror M_1 through a 6-mm diameter hole. The Brewster-angle potassium-chloride window which determined the polarization of laser power output could be rotated about the laser-tube axis in order to change the polarization vector. Under cw operation this laser produced a power output of ~10 W. Under Q-switched operation, peak power of ~10 kW was obtained in a pulse width of ~300 nsec. The laser pulses were measured with a Ge:Cu detector at 4.2°K. The detector output was taken across a 50-Ω load resistor in order to reduce the effects of lead capacitance. (A similar detector has been described in detail by Yardley and Moore[6] and is expected to have a response time of less than 20 nsec.) Under Q-switched operation, due to absence of competition among the rotational lines of a vibrational band, it was seen that both the P and R branches of the 00^01-10^00 and 00^01-02^00 vibrational bands oscillate at

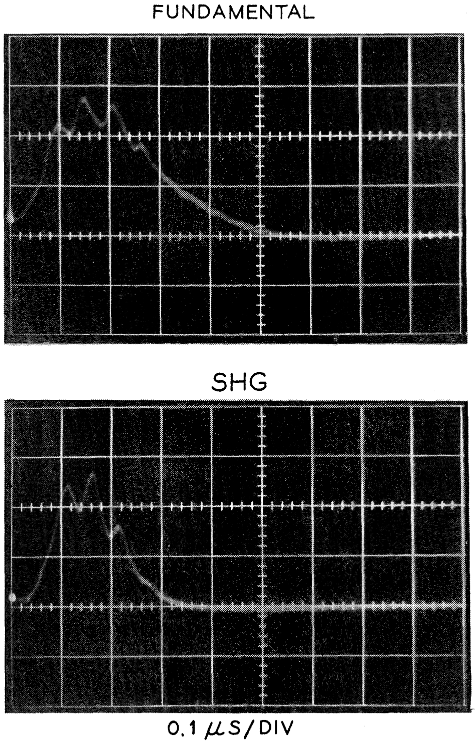

FIG. 2. Q-switched laser pulse at 10.6 μ and SHG pulse at 5.3 μ [$P_{10.6\,\mu}$ (peak) ≈10 kW, $P_{5.3\,\mu}$ (peak) ≈10 W].

the same time. Thus, care was taken to isolate the $P(20)$ transition of the 00^01-10^00 band of CO_2 for measurement of nonlinear coefficients of various materials (under Q-switched operation) in order to obtain unambiguous results.

To check the response time of the Ge:Cu detector, phase-matched SHG was obtained in a 3.5-mm long Te crystal under Q-switched operation which resulted in peak 5.3-μ power of the order of 10 W. Figure 2 shows a laser pulse at 10.6 μ and SHG pulse at 5.3 μ. As expected, the SHG pulse is narrower than the fundamental pulse, and we believe that the pulse widths seen in Fig. 2 are real. Under these experimental conditions 3ω generation due to $\omega+2\omega$ mixing was also observed. The third harmonic at 3.53 μ is strongly absorbed in Te since its intrinsic band gap lies at 3.82 μ for $E\perp c$.[7] Here E_ω was polarized in the y direction, $E_{2\omega}$ was polarized along in the x direction as in Ref. 1, and $E_{3\omega}$ was polarized along the y axis and was not phase matched. The power $P_{3\omega}$ emerging from the crystal is generated in approximately one absorption length of Te at the exit surface. (The absorption length is comparable to the coherence length.[7]) $P_{3\omega}$ of about 0.1 μW peak was measured.

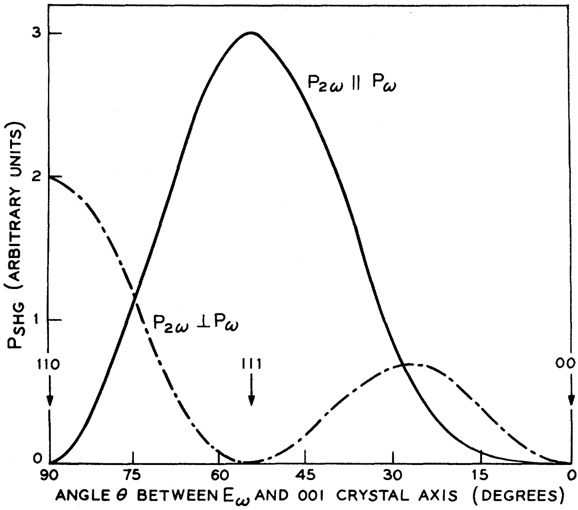

FIG. 3. Experimentally observed SHG from a 110 slab of InAs as a function of angle between the 001 axis and E_ω. (E_ω is in the plane 110.)

Nonphase-matched SHG in $\bar{4}3m$ single crystals GaAs, InAs, ZnS, CdTe, ZnSe, and ZnTe was obtained with E_ω polarized along the 111 direction and also along the 110 direction. In the first case E_ω and $E_{2\omega}$ are both polarized along the 111 direction. In the second case $E_{2\omega}$ will be normal to E_ω. (That this must be so can be seen from the symmetry of the nonlinear susceptibility matrix.) In Fig. 3 we have plotted $P_{2\omega} \parallel P_\omega$ and $P_{2\omega} \perp P_\omega$ from an InAs 110 slab as it is rotated about the 110 axis (direction of propagation of P_ω and $P_{2\omega}$). As expected we see the $P_{2\omega}{}^{\parallel} \propto \sin^4\theta\cos^2\theta$ and $P_{2\omega}{}^{\perp} \propto \sin^2\theta(1-3\cos^2\theta)^2$ behavior where θ is the angle between E_ω and the 001 direction. (Theoretical curve is not shown in Fig. 3.) The 111, 110, and 001 directions are marked on Fig. 3. Similar data have been reported for GaAs reflection SHG experiment in Ref. 2. Other materials of $\bar{4}3m$ symmetry examined here show similar behavior. Quantiative results on nonlinear coefficient d_{14} for these materials are given in Table I. The l_{coh} used for calculating the nonlinear optical coefficient is given together with how it was obtained. In some materials in which SHG is reported in this paper, a simple Maker experiment[8] is difficult because of very small dispersion between 5.3 and 10.6 μ and the resultant long l_{coh}. (For example, to make a meaningful measure-

Table I. Nonlinear coefficients and coherence lengths from SHG experiments at 10.6 μ.

Material	l_{coh} [a] (microns) Measured	Calculated	Nonlinear coefficient (10^{-7} esu)	$\delta_{ijk}/(4\pi)^3$ [b] (10^{-9} esu)
		$\bar{4}3m$		
GaAs	$110 \pm 10^{c,d}$		d_{14} 8.8 ± 3.0	0.93
InAs	60 ± 10^{c}	63^{e}	10.0 ± 3.0	0.84
ZnS	$53 \pm 5^{c,d}$	52^{f}	0.73 ± 0.2	1.25
ZnSe		126^{f}	1.87 ± 0.7	1.65
ZnTe	290 ± 50^{c}		2.2 ± 0.8	1.6
CdTe		$235^{e,f}$	4.0 ± 1.5	1.71
		$6mm$		
ZnS	d_{33} 52 ± 3^{c}		d_{33} 0.89 ± 0.3	1.57
	d_{31} 51 ± 3^{c}		d_{31} 0.45 ± 0.15	0.79
	d_{15} 53 ± 3^{c}		d_{15} 0.51 ± 0.2	0.9
CdS	d_{33} 67 ± 7^{c}		d_{33} 1.05 ± 0.3	1.3
	d_{31} 50 ± 5^{c}		d_{31} 0.63 ± 0.15	0.77
	d_{15} 73 ± 7^{c}		d_{15} 0.69 ± 0.17	0.86
CdSe	d_{33} 120 ± 10^{c}	g	d_{33} 1.3 ± 0.3	1.23
	d_{31} 64 ± 6^{c}		d_{31} 0.68 ± 0.15	0.63
	d_{15} 152 ± 10^{c}		d_{15} 0.74 ± 0.18	0.68
		32		
Se	phase matched[h]		d_{11} 1.9 ± 1.0	0.51

[a] $l_{\text{coh}} = \lambda_{\text{fund}}/[4(n_{\text{SHG}} - n_{\text{fund}})]$.

[b] See R. C. Miller, Appl. Phys. Letters 5, 17 (1965).

[c] Maker experiment (Ref. 8).

[d] Reflection phase-match experiment of G. D. Boyd and C. K. N. Patel, to be published.

[e] From index-of-refraction data of O. G. Lorimor and W. G. Spitzer, J. Appl. Phys. 36, 1841 (1965).

[f] From index-of-refraction data of IRTRAN-2 (polycrystalline ZnS), IRTRAN-4 (polycrystalline ZnSe), and IRTRAN-6 (polycrystalline CdTe) (Eastman Kodak Co., Rochester, New York).

[g] No refractive index measurements exist up to 10 μ for CdSe. However, our l_{coh} measurements indicate that CdSe is a positive birefringent material in agreement with short-wavelength work of W. L. Bond, J. Appl. Phys. 36, 1674 (1965).

[h] $l_{\text{Se}} \approx 0.7$ mm phase matched at $\theta_m \approx 10°$.

ment of l_{coh} in GaAs from the Maker experiment, the crystal has to be ~2 cm long.) The l_{coh} for GaAs and ZnS are also obtained from multiple-reflection phase-matching experiments.[9] The coherence lengths for some of these materials could be obtained from index-of-refraction data,[10] and these are given for comparison. In addition, we have given the quantity $\delta_{ijk}/(4\pi)^3$ which qualitatively compares the nonlinear coefficient of different materials. (See Miller[11] for details of this method of comparison.) It can be seen that within the framework of Miller's phenomenological theory,[11] a qualitative agreement exists.

In addition, under Q-switched operation, $\omega + 2\omega$ mixing and SHG from 2ω was also obtained in CdTe. 2ω was obtained from a 3.5-mm long phase-matched tellurium crystal (see above details). Peak $P_{3\omega}$ (at 3.53 μ) of about 1 μW and $P_{4\omega}$ (at 2.65 μ) of about 0.01 μW were obtained.

It is interesting to note that SHG was also obtained in IRTRAN-4 which is hot-pressed polycrystalline ZnSe, and in IRTRAN-6 which is polycrystalline CdTe. As expected, the $P_{2\omega}$ was randomly polarized, and was dependent upon the position of P_{ω} on the sample. With IR-6, the SHG obtained was about half of that in a single crystal sample of CdTe.

Results on $6mm$ crystals ZnS, CdS, and CdSe are given in Table I. The measured l_{coh} was obtained from the Maker experiment. Since no index-of-refraction data are available at long wavelengths, the coherence-length data yields the dispersion between 5.3 and 10.6 μ, and also the birefringence at 10.6 μ. It can be seen that for ZnS, CdS, and CdSe, within our experimental accuracy, $d_{31} \approx d_{15}$ in accordance with Kleinman's symmetry conditions.[12] (For CdS, these were verified at 6943 Å by

Miller, Kleinman, and Savage.[3]) Also, it should be noticed that for ZnS which occurs with zinc blende as well as hexagonal structure, the largest of the nonlinear coefficients, i.e., d_{14} for zinc blende ZnS and d_{33} for hexagonal ZnS, are nearly equal.

Trigonal-crystal selenium (space group $P3_{1,2}21$) is somewhat more interesting as compared with the crystals discussed above because phase matching is possible. (Thus Se is the second such nonlinear crystal at 10.6 μ, the first being Te.[1]) No reliable dispersion curves or birefringence data exist for single-crystal selenium other than data of Caldwell and Fan.[7] Phase matching was achieved at $\theta_m \approx 10°$ with the fundamental E vector polarized in the yz plane at θ_m from the y axis. Then the second harmonic is polarized along the x axis. [See Eq. (1) of Ref. 1 for an explanation.] Because of the large birefringence ($n^o = 2.78 \pm 0.02$, $n^e = 2.58 \pm 0.02$),[7] phase-matched SHG and other parametric experiments can be carried out up to wavelengths as short as 8000 Å. The accuracy of the nonlinear coefficient measurement for selenium is poor (possible error ~50%) because large single-crystal samples of Se are difficult to obtain.

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CRYSTAL STRUCTURE OF DEUTERIUM AT LOW TEMPERATURES*

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Previous structure determinations of normal deuterium are in apparent conflict. Kogan and co-workers[1] analyzed their earliest x-ray and neutron diffraction measurements at helium temperatures in terms of a body-centered tetragonal (bct) structure. Their latest x-ray studies,[2] however, suggest a structure which is hexagonal closest packed (hcp). Curzon and Pawlowicz[3] obtained electron diffraction patterns at about 7°K which they indexed on the basis of a face-centered cubic (fcc) lattice. Mucker and collaborators[4] at Ohio State recently reported neutron diffraction studies of deuterium at 13°K which clearly show the hcp structure.

The disagreements may have arisen because some of the studies[2,4] were made on bulk solid condensed in a cell and others[1,3] were made on thin layers of deuterium condensed on cold substrates. These substrates apparently cause crystallites to form with preferred orientations such that the intensities of the diffraction lines are altered. Recently it was discovered[5,6] that the structure of hydrogen near 1.3°K can be either fcc or hcp, depending upon the ortho-para ratio. The question of whether deuterium has a similar phase change prompted the present study by x-ray diffraction of solid deuterium.

In the hydrogen work, the temperature of the structure change was found to decrease with decreasing concentration of orthohydrogen (lowest rotational level $J = 1$) and to occur near the λ anomaly in specific heat.[7] An analogous

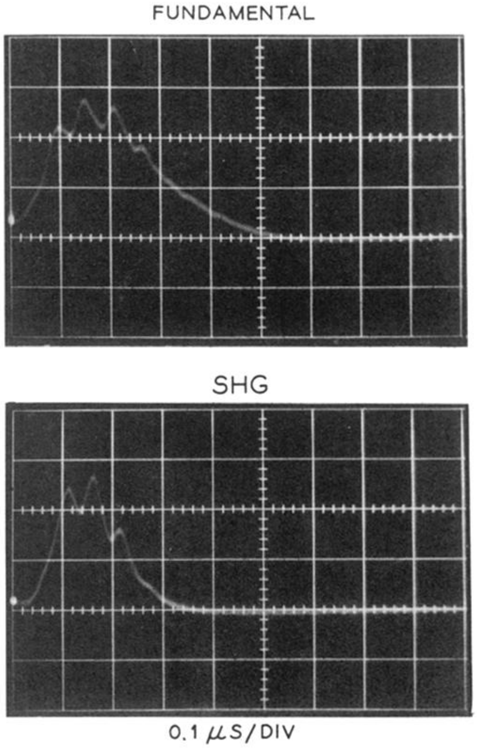

FIG. 2. Q-switched laser pulse at 10.6 μ and SHG pulse at 5.3 μ [$P_{10.6\,\mu}$ (peak) $\approx$10 kW, $P_{5.3\,\mu}$ (peak) $\approx$10 W].