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## Further Measurements of Absolute Signs of Second-Harmonic-Generation Coefficients of Piezoelectric Crystals

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(Received 7 February 1972)

The signs of the second-harmonic-generation (SHG) coefficients have been determined for SiC ( $d_{31+}$ ,  $d_{33-}$ ), AgGaS<sub>2</sub> ( $d_{36+}$ ), ZnGeP<sub>2</sub> ( $d_{36+}$ ), PbTiO<sub>3</sub> ( $d_{31-}$ ,  $d_{33+}$ ), Ba<sub>0.5</sub>Sr<sub>0.5</sub>Nb<sub>2</sub>O<sub>6</sub> ( $d_{31-}$ ,  $d_{33-}$ ), and PbNb<sub>4</sub>O<sub>11</sub> ( $d_{32-}$ ,  $d_{33-}$ ). Where comparisons between theory and experiment can be made, the agreement is good except for PbTiO<sub>3</sub>. In addition, the phases of the SHG coefficients for CdTe, CdSe, and ZnTe have been redetermined in a spectral region where the crystals are transparent and the phases were found to agree with expectations—all  $d$ 's positive except  $d_{31}$  for CdSe.

### I. INTRODUCTION

This paper describes some recent determinations of the absolute signs of the second-harmonic-generation (SHG) coefficients  $d_{ij}$  of a number of piezoelectric crystals not previously measured. In addition, some crystals studied earlier<sup>1</sup> in spectral regions in which the nonlinear coefficients were found to be complex (presumably due to absorption effects) have been remeasured at longer wavelengths where these effects are expected to be absent. Of particular interest are the results on SiC, PbTiO<sub>3</sub>, and AgGaS<sub>2</sub>, all of which are relevant to important tests of the theories of  $d_{ij}$ .

The more successful of the earlier theories which considered the absolute signs and magnitudes of the SHG coefficients treated the tetrahedrally coordinated compounds (e. g., III-V compounds) and predicted positive bond nonlinearities with the positive direction defined from the metal to the non-metal atom.<sup>2–4</sup> Subsequently, a dependence of the nonlinearity on the relative covalent radii of the two atoms making up the bond was presented by Levine<sup>5</sup> to explain the negative  $d_{33}$ 's observed for

ZnO, LiGaO<sub>2</sub>, and BeO, the  $+d_{11}$  for SiO<sub>2</sub>,<sup>1</sup> and the observed signs for both  $d$ 's of potassium dihydrogen phosphate (KDP).<sup>6</sup> This theory also predicts a negative  $d_{33}$  for SiC.<sup>5</sup>

More recently it has been reported that  $d_{14}$  for CuCl is negative,<sup>7</sup> and hence in conflict with Refs. 2–5. It is well known that the  $3d$  electrons in Cu are close in energy to the  $4s$  electrons and may therefore influence the magnitude and sign of the nonlinearity of Cu-containing compounds.<sup>8–10</sup> A somewhat similar situation exists between the  $5s$  and  $4d$  electrons in Ag; hence the interest in AgGaS<sub>2</sub>.<sup>8–10</sup> Most recently Levine has shown<sup>10</sup> how to include contributions to the nonlinear susceptibility from the  $d$  electrons of Cu- and Ag-containing compounds. In particular,  $d_{14}$  for CuCl is predicted to be minus (as observed), and  $d_{36}$  for AgGaS<sub>2</sub> is expected to be positive.

Ferroelectric crystals BaTiO<sub>3</sub> and PbTiO<sub>3</sub> are isomorphous at room temperature; however, PbTiO<sub>3</sub> is characterized by an unusually large displacement of the Pb<sup>2+</sup> ions from their paraelectric prototype positions.<sup>11,12</sup> The contribution of the Pb<sup>2+</sup> ions to the nonlinearity of PbTiO<sub>3</sub> may there-

fore give rise to results different from those of  $\text{BaTiO}_3$ , where the  $\text{Ba}^{2+}$  ion displacements are small, and their contribution to the nonlinearity can be neglected.<sup>8</sup>

In the present paper, the absolute signs of the second-order nonlinear optical coefficients are presented for the first time for a hexagonal form of  $\text{SiC}$ ,  $\text{AgGaS}_2$ ,  $\text{ZnGeP}_2$ ,  $\text{PbTiO}_3$ ,  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ , and  $\text{PbNb}_4\text{O}_{11}$ . Crystals remeasured at longer wavelengths than previously<sup>1</sup> to eliminate absorption effects are  $\text{ZnTe}$ ,  $\text{CdTe}$ , and  $\text{CdSe}$ .

## II. EXPERIMENTAL TECHNIQUES

Most of the data obtained at  $1.06 \mu\text{m}$  were generated with a conventional repetitively  $Q$ -switched Nd-yttrium-aluminum-garnet (YAG) laser plus the usual ancillary equipment. The remaining data were obtained with a Chromatix Nd-YAG laser capable of generating laser fundamentals at 13 wavelengths from  $1.358$  to  $0.946 \mu\text{m}$ . As in earlier measurements,<sup>1</sup> the absolute signs of the  $d$ 's were determined via an interference experiment between a crystal of known absolute sign and the unknown mounted in series. The sign of the unknown coefficient is then deduced from the characteristics of the interference pattern as the dispersion of the medium between the two crystals is varied in a controlled manner by going from either a vacuum (1 torr) or 1 atm of He, to 1 atm of  $\text{CO}_2$ . These techniques are described adequately elsewhere.<sup>1,13</sup>

In order to interpret the results, the absolute orientation of each crystal is required. This information can in principle be obtained through piezoelectric, pyroelectric, and etch tests, and through x-ray studies. The latter method is of course the only one that relates to the atom positions in the crystal and is therefore required for most comparisons between theory and experiment.

## III. RESULTS

The signs for crystals not previously measured are summarized in Table I, which also includes information on the method employed to determine the absolute orientation.

### A. SiC

The hexagonal SiC crystal measured was the same one employed earlier by Singh *et al.*,<sup>14</sup> who determined the magnitudes of the two coefficients and found them to be smaller than predicted.<sup>5</sup> The crystal studied was a hexagonal form of unknown polytype; however, the birefringence suggests that it was a  $15R$  polytype.<sup>15</sup> The relative signs given in Table I coupled with the magnitudes obtained by Singh *et al.* show that  $d_{33}/d_{31} = -1.7 \pm 0.3$  and hence in satisfactory agreement with the  $-2.0$  prediction from symmetry arguments.<sup>16</sup> To determine the absolute orientation, a  $\text{K}_3\text{Fe}(\text{CN})_6$  etch<sup>17</sup> was em-

ployed which enables one to relate the sign of  $d_{ij}$  to the absolute atomic configuration. It is concluded that  $d_{33}$  is indeed negative as predicted by Levine.<sup>5</sup> This is therefore the sixth example<sup>1,6</sup> where the sign of  $d$  reverses owing to the quite different covalent radii for the two atoms making up the crystal.

### B. $\text{PbTiO}_3$

The single-domain crystal of  $\text{PbTiO}_3$  measured showed that  $d_{33}$  and  $d_{31}$  are positive and negative, respectively, where the positive  $z$  direction is defined by the direction of the spontaneous polarization  $P_s$ . As discussed earlier by Singh *et al.*,<sup>18</sup> who had determined the magnitudes of  $d_{31}$  and  $d_{33}$  for this crystal prior to the present study, the sum  $2|\delta_{31}| + |\delta_{33}|$  is in poor agreement with a general formulation for polar crystals due to Jerphagnon which states that<sup>19,20</sup>

$$\delta_v \equiv \delta_{31} + \delta_{32} + \delta_{33} = -(1.0 \pm 0.3) \times 10^{-7} P_s \text{ esu}, \quad (1)$$

where  $P_s$  is the spontaneous polarization in  $\mu\text{C}/\text{cm}^2$  and  $\delta$  (in the full notation) is defined by<sup>21</sup>

$$d_{ijk} = \delta_{ijk} \chi_{ii}^{2\omega} \chi_{jj}^{\omega} \chi_{kk}^{\omega}. \quad (2)$$

The optical susceptibilities  $\chi_{ll} = (n_l^2 - 1)/4\pi$  are along the principal index direction  $l$  at the frequency given by the superscript. When the present absolute-sign measurements are combined with the magnitudes determined earlier,<sup>18</sup> we conclude that  $\delta_v = [-2(1.9 \pm 0.25) + (0.4 \pm 0.04)]\delta_{11}(\text{SiO}_2)$ , or with  $\delta_{11}(\text{SiO}_2) = 6.7 \times 10^{-7} \text{ esu}$ ,<sup>22,23</sup>  $\delta_v = -23 \times 10^{-7} \text{ esu}$ . This value for  $\delta_v$  therefore corresponds to  $P_s = 23 \mu\text{C}/\text{cm}^2$ , which is substantially less than the directly measured values of 57 and  $75 \mu\text{C}/\text{cm}^2$ .<sup>24,25</sup> This discrepancy between  $\delta_v$  and  $P_s$  is the largest known to the present authors.

Application of the Levine<sup>5</sup> bond charge model of nonlinearities in a manner similar to that used earlier<sup>8</sup> for  $\text{BaTiO}_3$  leads one to expect that both  $d_{31}$  and  $d_{33}$  for  $\text{PbTiO}_3$  should be negative, contrary to the present results. This approach ignores contributions from the Ba-O and Pb-O bonds, but it can easily be modified in a formal way to include these bonds. In the case of  $\text{PbTiO}_3$ , the displacements of the  $\text{Pb}^{2+}$  ions from their paraelectric prototype positions are unusually large<sup>11,12</sup> ( $0.47 \text{ \AA}$ ), which argues in favor of including the Pb-O bonds. This problem has yet to be solved properly; however, it appears that the Pb-O bonds may have a negative nonlinearity, i. e., opposite to that of the Ti-O bonds.

The present results suggest that it would be interesting to study the mixed  $\text{Pb}_x\text{Ba}_{1-x}\text{TiO}_3$  system. It should be noted that  $\text{PbTiO}_3$  is the first ferroelectric-type material found with a positive  $d_{33}$ .

TABLE I. Signs of SHG coefficients for crystals not previously measured.

Crystal	$\lambda_1$ ( $\mu\text{m}$ )	Orientation				Ref.
		$d_{31}$	$d_{32}$	$d_{33}$	$d_{36}$	
SiC	1.06	+	-		E	17, a
AgGaS <sub>2</sub>	1.36			+	$\pi$	a
ZnGeP <sub>2</sub>	1.36				$\pi$	a
PbTiO <sub>3</sub>	1.06	-		+	$P_s$	a
Ba <sub>0.5</sub> Sr <sub>0.5</sub> Nb <sub>2</sub> O <sub>6</sub>	1.06	-		-	$P_s$	a
PbNb <sub>4</sub> O <sub>11</sub>	1.06	b	-	-	$\pi, P$	a

<sup>a</sup>E, etch test;  $\pi$ , piezoelectric test (see Ref. 29 for sign conventions);  $P_s$ , electric-field-oriented spontaneous polarization;  $P$ , pyroelectric test [a positive charge develops on the (001) face on cooling, from which the outward normal is the positive [001];  $dP_s/dT$  is assumed to be negative].

<sup>b</sup>Not determined.

### C. Chalcopyrites

The sign of the  $d_{36}$  nonlinear coefficient for the two chalcopyrite-type crystals ZnGeP<sub>2</sub><sup>26</sup> and AgGaS<sub>2</sub><sup>27,28</sup> has been determined relative to the sign of the piezoelectric effect. Both of these tetrahedrally coordinated crystals have large nonlinear optical coefficients that make them very promising for nonlinear optical applications in the infrared.<sup>26-28</sup> As is common practice,<sup>29</sup> the +z direction is defined as the outward normal from the z-cut face that develops a positive charge upon extension along a [110]. In each case it is found that  $d_{36}$  is real and positive when the fundamental wavelengths is 1.358  $\mu$ . Comparison with the detailed predictions of Levine<sup>10</sup> must await an absolute crystal structure determination; however, these data do not suggest a sign reversal for  $d_{36}$  due to Ag, in agreement with Levine.

### D. Miscellaneous Other Crystals

Several single-domain crystals of Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub> (SBN) have been studied with  $x \approx 0.5$  and 0.75. In each case the ratio  $\delta_{33}/\delta_{31} = +2.3 \pm 0.1$ . The signs of the coefficients relative to  $P_s$  and their magnitudes relative to  $d_{11}$  of quartz were measured for one crystal with  $x \approx 0.5$ . It was found that  $d_{33} = -39 \times 10^{-9}$  esu and  $d_{31} = -19 \times 10^{-9}$  esu, where  $|d_{11}(\text{SiO}_2)|$  was taken as  $8.7 \times 10^{-10}$  esu.<sup>22,23</sup> These values for SBN are slightly larger than those found earlier<sup>30</sup> [ $|d_{31}| = (12 \pm 4) \times 10^{-9}$  esu and  $|d_{33}| = (31 \pm 9) \times 10^{-9}$  esu]; however, this difference may be due to a compositional variation between the two SBN crystals studied. The ferroelectric Curie temperature of the crystal measured in the present study was  $\approx 104^\circ\text{C}$ , in satisfactory agreement with earlier work.<sup>31</sup> From the work of Jerphagnon,<sup>19</sup> Eq. (1), one therefore deduces  $P_s = 22 \pm 7 \mu\text{C}/\text{cm}^2$ , since  $\delta_v = -22 \times 10^{-7}$  esu. This value of  $P_s$  is in excellent

agreement with that determined directly by Camlibel, who found  $P_s = 25 \pm 1 \mu\text{C}/\text{cm}^2$ .<sup>32</sup>

Measurements of the signs of  $d_{32}$  and  $d_{33}$  of a crystal of PbNb<sub>4</sub>O<sub>11</sub> relative to an absolute positive direction determined by the piezoelectric effect showed that both coefficients were negative. The sample orientation was such that the sign of  $d_{31}$  could not be obtained. The magnitudes of the  $d$ 's for PbNb<sub>4</sub>O<sub>11</sub> have been determined earlier.<sup>33</sup>

### E. Absorption Effects

Earlier attempts at absolute-sign determinations for ZnTe, CdTe, and CdSe<sup>1</sup> using a 1.06- $\mu\text{m}$  fundamental were subject to some uncertainty due to effects resulting from absorption at the second-harmonic frequency. These crystals have been reexamined at a fundamental wavelength of either 1.318 or 1.358  $\mu\text{m}$ , thereby eliminating the possibility of significant phase shifts in the measured quantity due to complex refractive indices. In these experiments the quantity determined is the phase angle between the second-harmonic wave and the fundamental squared at the exit of the unknown crystal (plus or minus  $\pi$ ). From this measurement one obtains<sup>1</sup>

$$(\varphi_{ki})_{\text{out}} = \varphi_{ki}^a + \varphi_{ki} \quad (3)$$

In this expression,  $\varphi_{ki}$  is the quantity of interest, which is defined by

$$d_{ki} = d_{ki}^0 e^{i\varphi_{ki}}, \quad (4)$$

where  $d_{ki}^0$  is real and positive, and  $\varphi_{ki}^a$  is the phase shift due directly to the complex refractive indices as discussed below. When the crystal is opaque to the harmonic, the part of the expression for the second-harmonic amplitude which determines  $\varphi_{ki}^a$  is given by<sup>1</sup>

$$E_2 \propto [(n_2^* - n_1^*)(n_1^* + 1)^2(n_2^* + 1)]^{-1} \quad (5)$$

The quantities  $n_i^*$  are the complex refractive indices at the frequency indicated by the subscripts. Thus  $\varphi_{ki}^a$  is determined by Eq. (5) and is equal to zero for all real  $n_i$ .

Crystals of ZnTe, CdTe, and CdSe have been re-

TABLE II. Signs of SHG coefficients for crystals re-measured in the absence of absorption effects.

Crystal	$\lambda_1$ ( $\mu\text{m}$ )	Orientation			Ref.	
		$d_{14}$	$d_{31}$	$d_{33}$		
ZnTe	1.318	+			E(x)	b
CdTe	1.358	+			$\pi$	a
CdSe	1.358		-	+	$\pi\text{E}(x)$	a, b

<sup>a</sup>See Table I. Also, (x) means method related to absolute structure determined by x-ray analyses.

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measured at wavelengths where  $\varphi^a$  can be ignored, and the results, which are summarized in Table II, are in agreement with predictions.<sup>3-5,9</sup>

It should be noted that  $(\varphi_{14})_{\text{ext}} = \pm \pi$  given earlier<sup>1</sup> by the present authors for CdTe ( $\lambda_1 = 1.064 \mu\text{m}$ ) is believed to be in error. The orientation of the sample had been determined by etch tests<sup>1</sup> which we have found in subsequent studies to be unreliable. Therefore, for the present results, a piezoelectric test was employed to determine  $+ [111]$ . It was assumed that CdTe has a positive piezoelectric coefficient like all the other II-VI compounds measured to date.<sup>34</sup> Also a positive piezoelectric coefficient is predicted by the theory of Phillips and

Van Vechten.<sup>35</sup> We now conclude that  $(\varphi_{14})_{\text{ext}} = 0$  for CdTe for both  $\lambda_1 = 1.064$  and  $1.358 \mu\text{m}$ .

#### ACKNOWLEDGMENTS

The authors would like to express their appreciation to those who contributed some of the crystals to this research; in particular, S. Singh (SiC and  $\text{PbNb}_4\text{O}_{11}$ ), E. Buehler ( $\text{ZnGeP}_2$ ), H. Kasper ( $\text{AgGaS}_2$ ), and J. P. Remeika ( $\text{PbTiO}_3$ ). The high-quality optical finishes on many of the crystals studied were produced by S. Bortas. Also, it is a pleasure to acknowledge fruitful discussions with Dr. G. D. Boyd, Dr. B. F. Levine, Dr. S. Singh, and Dr. J. P. van der Ziel.

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