## Crystal Structure, Linear and Nonlinear Optical Properties of Ca(IO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O\*

BY B. MOROSIN

Sandia Laboratories, Albuquerque, New Mexico 87115, U.S.A.

AND J.G. BERGMAN AND G.R. CRANE

Bell Telephone Laboratories Incorporated, Holmdel, New Jersey 07733, U.S.A.

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The room-temperature crystal structure of Ca(IO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O has been independently determined and refined (R=0.032) by a full-matrix least-squares method using 1544 Mo K $\alpha$  counter-measured intensity data. This material crystallizes in space group Fdd2 with eight molecules in a unit cell of dimensions  $a_0 = 14.829$  (7),  $b_0 = 22.980$  (9) and  $c_0 = 6.383$  (3) Å. The calcium ions are coordinated to the six water oxygen and to two iodate oxygen atoms in a distorted Archimedian antiprism with edges 2.85-3.15 Å; the trigonal, pyramidal iodate ions [I–O, 1.81 (2) Å; O–I–O, 98.2 (7)°] are held in the lattice by a network of hydrogen bonds and arranged to give a highly distorted octahedral environment about the iodine (long I–O separations are 2.82-2.90 Å). The indices of refraction at  $0.53\mu$  are  $n_x = 1.625$ ,  $n_y = 1.654$ ,  $n_z = 1.688$ . The nonlinear coefficients  $d_{311}$ ,  $d_{322}$ ,  $d_{333}$ ,  $d_{113}$ ,  $d_{223}$ , measured relative to  $d_{333}$  (LiIO<sub>3</sub>) are respectively 0.14, 0.015, 0.40, 0.11, 0.007. The nonlinear bond polarizability  $\beta$  for the long ( $\sim 2.8$  Å) I–O bond is found to be twice that of the short ( $\sim 1.8$  Å) I–O bond.

#### Introduction

Noncentrosymmetric crystals that can be grown with good optical quality are of interest for their applications in second harmonic generation (SHG) and optical parametric generation. Development and treatment of nonlinear optical materials and their applications can be found in reviews by Bergman & Kurtz (1970), and Hulme (1973). To date, a number of alkali iodates as well as iodic acid have been shown to have the desired large nonlinear optical coefficients and have been shown to be phase matchable (Kurtz, Perry & Bergman, 1968; Bergman, Boyd, Ashkin & Kurtz, 1969). Our structure studies, completed independently of Braibanti, Lanfredi, Pellinghelli & Tiripicchio (1971; hereafter BLPT), indicated that  $Ca(IO_3)$ ,  $6H_2O$  crystallizes in a noncentrosymmetrical space group; furthermore, SHG tests of powdered samples (Kurtz & Perry, 1968) showed that the material was phase-matchable, which prompted examination of its optical properties.

Surprisingly, studies relating structure and optical nonlinearities in LiIO<sub>3</sub> and HIO<sub>3</sub> (Jeggo, 1970) showed that, of the two sets of iodine-oxygen bonds, the longer set (I-O  $\sim 2.8$  Å, essentially a van der Waals interaction) contributes twice as much to the optical nonlinearity as does the shorter set (I-O  $\sim 1.8$  Å). Since only 3 nonlinear coefficients (all of which are approximately equal in magnitude) have ever been measured on iodate compounds, one would like to test further this relation between bond distance and nonlinear susceptibility in other iodate compounds.

#### Crystal structure

Because the preliminary results of Cingi, Emiliani & Guastini (1967) were overlooked, a structure determination on  $Ca(IO_3)_2.6H_2O$  was initiated by one of the authors several years ago. It was felt that an article pointing out the potential usefulness of noncentrosymmetric crystals for SHG was desirable. Recently, BLPT published their structure results, employing a different selection of axes; however, the structures are similar. Their residual index of 0.118 on data from photometrically-measured, integrated photographs appears rather high and, thus, warrants our reporting the present results.

### (a) Experimental

The space group Fdd2 was established on the basis of systematic extinctions (h+k, k+l) and hence l+hodd for hkl,  $k+l \neq 4n$  for 0kl, and  $h+l \neq 4n$  for h0lreflections absent). Absence of the center of symmetry was confirmed by the presence of a piezoelectric response and optical SHG.

The lattice constants  $a_0 = 14.829(7)$ ,  $b_0 = 22.980(9)$ , and  $c_0 = 6.383(3)$  Å [selected according to Donnay's (1943) rules] were obtained on our diffractometer using Mo K $\alpha$  radiation. With eight molecules of Ca(IO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O per cell, the calculated density is 3.05 g cm<sup>-3</sup>. (BLPT reports 2.97 g cm<sup>-3</sup> determined by the pycnometer method.) Since the space group was noncentrosymmetric, a set of Mo K $\alpha$  intensity data was measured which contained both positive and negative values of *l*. These 1544 intensity data were measured with a scintillation counter employing pulse-height discrimination; the  $\theta$ -2 $\theta$  scan technique was used with

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a scan speed of  $\frac{1}{2}$  deg min<sup>-1</sup> over the interval  $2\theta_{\lambda_1} - 0.80^\circ$  to  $2\theta_{\lambda_2} + 0.80^\circ$ . Of these data, 23 were measured to be less than  $3\sigma$ , where  $\sigma = \sqrt{(N_{SC} + K^2 \cdot N_B)}$  in which  $N_{SC}$ , N<sub>B</sub>, and K are the total scan count, background counts, and ratio of the scan to background time respectively. These particular data were, therefore, assigned a value equal to  $3\sigma$  and considered to be unobserved in subsequent calculations.

Absorption corrections  $(\mu_{Mo} \kappa_{\alpha} = 63.4 \text{ cm}^{-1})$  were applied to the intensity date for the crystal specimen bounded by large (112) and small (100) and (010) faces and of dimensions  $0.44 \times 0.34 \times 0.28$  mm (mounted on the longest direction [100]). Lorentz and polarization factors were applied and structure factors calculated using scattering factors from Table 3.3.1*B* (p. 210) for Ca<sup>2+</sup> and I and from Table 3.3.1*A* (p. 202) for O and H and dispersion corrections for Ca(0.2 and 0.4) and I(-6 and 2.2) from Table 3.3.2*C* (p. 215) of International Tables for X-ray Crystallography (1962).

For space group *Fdd2*, there are 16-fold general positions $(x, y, z; \bar{x}, y, z; \frac{1}{4} - x, \frac{1}{4} + y, \frac{3}{4} + z; \frac{1}{4} + x, \frac{1}{4} - y, \frac{3}{4} + z)^*$ on which the iodine and oxygen atoms are situated as well as eightfold special positions on the twofold axis  $(0,0,z \text{ and } \frac{1}{4}, \frac{3}{4}, \frac{3}{4}+z)$  on which the calcium ion is situated; both position sets are combined with the face centering of  $(0,0,0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; and \frac{1}{2}, \frac{1}{2}, 0)$ . Positional parameters for the iodine atoms were obtained from a Patterson synthesis and those for the other atoms from a subsequent Fourier synthesis. Initially only reflections with positive value of l were employed in the least-squares refinement of the atomic positional and isotropic thermal parameters (the z parameter of I was set to zero). The value of the residual index R, where  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , was reduced to 0.049 using dispersion corrections introduced by the method of Templeton (1955). The alternate absolute configuration yielded an R value of 0.047. The value of the  $\Re$  index ratio is  $\Re = 0.049/0.047 = 1.04$ ; hence, on the basis of the 844 positive *l* reflections used, the hypothesis that the first absolute configuration is correct can be rejected at a level much lower than 0.005 (Hamilton, 1965). This choice was confirmed by comparison of 74 pairs (+1)of reflections for which the structure factor with and without dispersion resulted in a 5% difference. The

\* This choice of symmetry operators resulted from our method of calculating the absolute configurations.

entire data set (except 040 which was considered to suffer secondary extinction) were subjected to leastsquares refinement with anisotropic thermal parameters yielding R=0.032; parameters obtained are listed in Table 1.\* The average dispersion corrected observed structure factors are compared with the calculated values in Table 2.

## (b) Results

The present refined atomic parameters differ by only a maximum of five pooled standard deviations from values obtained by BLPT; however, the R value is significantly smaller and the values for the I-O bond separations (Table 3) show less spread than values of 1.78, 1.85 and 1.90 Å obtained by BLPT. Hence, the following results are described only in terms of the present values.

The coordination about the calcium ion consists of eight oxygen atoms (six water oxygen and two iodate oxygen atoms) situated in a distorted Archimedian antiprism with edges 2.85 to 3.15 Å (Table 3). The pseudo-fourfold axes of these antiprisms are situated in the *ab* plane; for example, in Fig. 1(*a*), using the calcium ion located at the center  $(\frac{1}{4}, \frac{1}{4})$ , the pseudo-fourfold axis lies between the Ca-O(2) and Ca-O(6) vectors.

The separations in the iodate ion are typical of these found in other iodates: the bonds average 1.82 Å with nonbonding neighboring iodate-oxygen interactions near 2.8-2.9 Å (summarized by Keve, Abrahams & Bernstein, 1971). In such an arrangement, the iodine

<sup>\*</sup> After this paper was accepted, the authors had a discussion with S. C. Abrahams concerning the possibility of achieving either (a) an  $\mathcal{R}$  index ratio equal to 1.0 (the equal R values resulting from different sets of atomic coordinates) or (b) even the incorrect absolute configuration because of unequal convergence of the two least-squares refinements when only one set of reflections (as in the present case, +1) are used in determining R. Hence, the total data set was subjected to additional least-squares refinement which included, in addition, a correction for secondary extinction. The *R* index ratio (0.031/0.036 = 1.14) confirmed the above assignment of the configuration; interestingly, the ratio proved to be larger than that for the case in which only one data set (+1) was used (see text). This suggests that the preferred procedure for the selection of the absolute configuration in noncentrosymmetric structures should use the entire data set. The introduction of the secondary extinction correction did not alter the positional parameters shown in Table 1; a few thermal parameters changed in the last digit, always less than  $0.3 \times \sigma$ .

Table 1. Positional and thermal parameters for Ca(IO <sub>3</sub> )	)2.6H2O
Anisotropic thermal parameters are of the form $\exp\left[-\left(\frac{1}{2}\sum_{i=1}^{3}E_{i}\right)\right]$	$B_{i,a}^{\dagger}a_{i}^{\dagger}h_{i}h_{i}h_{i}h_{i}h_{i}h_{i}h_{i}h_{i$

	· ·								
	x	У	Z	$B_{11}$	B22	$B_{33}$	$B_{12}$	B <sub>13</sub>	$B_{23}$
Ca	0.0	0.0	0.312(1)	1.0 (2)	0.9(2)	1.0 (2)	_	-	-
I	0.0145 (1)	0.13939 (6)	0.0	0.94 (5)	1.05 (4)	0.91 (4)	0.01 (2)	-0.01(5)	-0.02(4)
O(1)	0.171(1)	0.074 (1)	0.871 (4)	1.5 (6)	1.8 (7)	1.6 (7)	-0.3(6)	0.4 (6)	0.3 (6)
O(2)	0.223(1)	0.184(1)	0.761(5)	1.8 (6)	1.1(5)	1.7 (7)	0.5 (6)	-0.3(7)	-0.1(7)
O(3)	0.234(1)	0.095 (1)	0.480(4)	1.3 (6)	$2 \cdot 1$ (7)	1.1 (7)	-0.2(6)	-0.1(6)	-0.1(6)
O(4)	0.165 (1)	0.007 (1)	0.220(3)	1.6 (7)	1.6 (7)	1.2 (8)	-0.1(7)	0.1(5)	-0.1(6)
O(5)	0.052(1)	0.098 (1)	0.406 (4)	1.5 (7)	1.9 (5)	1.2 (8)	0.0 (6)	-0.2(5)	-0.2(6)
O(6)	0.154 (2)	0.228(1)	0.374 (4)	2.4 (9)	2.3 (8)	1.5 (8)	0.5 (7)	0.3 (6)	0.5 (6)

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# Table 3. Bond angles and separations in $Ca(IO_3)_2.6H_2O$

(a) Calcium ion environment (e.s.d. Ca-O, 0.02; O-O, 0.03 Å; O-Ca-O, 0.7°)

Bond angles (°)

O(2)-Ca-O(2')

O(4)-Ca-O(4')

O(5)-Ca-O(5')

O(6)-Ca-O(6')

O(4)-Ca-O(6)

Separations (Å)

2.47

2.52

2.44

2.50

2 02

Ca - O(2)

Ca--O(4)

Ca - O(5)Ca - O(6)

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atom is in a highly distorted octahedral environment, which appears to be a common feature of crystalline iodates. One of the iodate oxygen atoms is involved in an electrostatic interaction with the calcium ion; all iodate oxygen atoms are hydrogen bonded. The accuracy of this determination is not sufficient to determine if such interactions change the particular value of the I–O separation.

Hydrogen bonding in this material is not uniquely defined by the short O–O separations [(Table 3(c)]. Each water molecule is situated adjacent to iodate oxygen atoms involving separations less than 2.95 Å; in addition there is one short interaction involving only water oxygen atoms, O(6)-O(4). This latter separation as well as O(5)-O(2) are edge separations of the calcium ion polyhedron. For two of the water molecules, O(4) and O(5), the shorter separations and corresponding angles suggest the more probable locations for the hydrogen bonds. For O(6), the nearest neighbors are about 0.1 Å more distant than those of O(4) and O(5). The shorter separation, as mentioned above, involves an edge of the calcium ion polyhedron. Although the two other separations, O(6)-O(2) and O(6)-O(1), may be the correct location for the

	J(4)-U(5)	2.92	O(2) - Ca - O(3)	/1.7
			O(4)-Ca-O(5)	72.1
(	D(4)-O(6)	2.85	O(2)-Ca- $O(4)$	72.4
0	O(4) - O(2)	2.94	O(5)-Ca-O(6)	78·7
(	O(5)–O(6)	3.15	O(5)-Ca-O(6)	7 <b>9</b> ·4
(	D(5)-O(6)	3.13	O(4)-Ca-O(2)	86.4
			O(2)-Ca-O(6)	113.6
(	O(5)-O(2)	2.85	O(4)–Ca–O(5)	114.9
(	O(6)-O(6)	3.03	O(2)-Ca-O(5)	133.9
			O(4)-Ca-O(6)	136.8
(	O(2) - O(2)	3.11	O(2)-Ca-O(6)	146.5
(b) 🛛	Iodate ion (e.s.d	. I–O, 0·02	Å; O–I–O, 0·7°)	
I	-O(1)	1.81	O(1) - I - O(2)	99·2
I	-O(2)	1.81	O(1) - I - O(3)	96.6
I	-O(3)	1.82	O(2) I O(3)	98.8
I	-O(1')	2.88	O(1) - I - O(1')	170.7
I	-O(4')	2.90	O(2) - I - O(4')	178.3
I	–O(5')	2.82	O(3)-I-O(5')	171.3
(c)	Water molecules	s (e.s.d. O-0	O, 0·03 Å; O−O−O, 0	ŀ9°)
(	O(4)–O(3)	2.80	O(3) - O(4) - O(1)	93.7
(	O(4) - O(1)	2.70	O(3) - O(4) - O(6)	76 <b>·2</b>
	., .,		O(1) - O(4) - O(6)	152.5
(	O(5)-O(3)	2.73	O(3) - O(5) - O(3')	104.5
(	O(5) - O(3')	2.68	O(3) - O(5) - O(2)	123.6
(	O(5) - O(2)	2.85	O(3')-O(5)-O(2)	130.6
(	O(6)-O(2)	<b>2</b> ·87	O(2) - O(6) - O(4)	173.1
(	O(6)–O(4)	<b>2</b> ·85	O(1) - O(6) - O(4)	100.4
(	O(6)-O(1)	2.93	O(2) - O(6) - O(1)	85.8

hydrogen bonds about this water, one is not able to eliminate the possibility of a bifurcated hydrogen bond similar to that found in several other hydrates (summarized in Morosin, 1967).

### **Optical properties**

### (a) Experimental

Ζ.

Single crystals ~5 mm on a side were grown from an aqueous solution (300 ml) over a period of 6 months by convectively cycling the solution from the nutrient region (temp. 35°C) to the crystal growth region (temp. 25°C). Indices of refraction at  $0.53\mu$ , as determined from index matching oils and birefringence measurements, are given in Table 4. It is seen that Ca(IO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O is negative biaxial. The twofold polar axis is z, the acute bisectrix x, and the obtuse bisectrix

### Table 4. Refractive indices of Ca(IO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O

Refractive		
index	At 0·53μ	At 1.06µ
$n_x$	1.625	1.582
ny	1.654	1.625
nz	1.688	1.653

78·2

152.7

152.3

74.7

69·2

The scheme for the array of nonlinear coefficients subject to mm2 symmetry is (Nye, 1964)

ſΟ	0	0	0	$d_{113}$	-07	
0	0	0	$d_{223}$	0	0	
$d_{311}$	$d_{322}$	<i>d</i> <sub>333</sub>	0	0	0	

Hence, the components of the nonlinear polarization at the second harmonic wavelength in terms of the Efields at the fundamental wavelength are given by (Bergman & Kurtz, 1970)

$$P_{x} = 2d_{113}E_{x}E_{z} \tag{1}$$

$$P_{y} = 2d_{223}E_{y}E_{z} \tag{2}$$

$$P_z = d_{311}E_x^2 + d_{322}E_y^2 + d_{333}E_z^2 . \tag{3}$$

The coefficients were measured relative to  $d_{333}$  of LiIO<sub>3</sub> by SHG experiments using a Q switched Nd-YAG laser operating at 1.06 $\mu$ . The experimental setup is shown in Fig. 2. Samples were prepared in the form of thin wedges (~5×2 mm,  $\theta$ =3.5°), which when translated along the wedge direction gave fringes (periodic maxima and minima in the observed second harmonic signal) allowing the determination of the coefficients  $d_{ijk}$  as well as their respective coherence lengths  $l_{ijk}$  (Fig. 3). The coherence length ( $l_{ijk}$ ) is related to the translational period t(t = distance between maxima or minima) and the wedge angle ( $\theta$ ) by

$$l_{ijk} = \frac{1}{2}t \tan \theta \,. \tag{4}$$

Observed coherence lengths are given in Table 5.

## Table 5. Experimental SHG results on $Ca(IO_3)_2.6H_2O$ relative to $(d_{333})LiIO_3$

		Coherence	Rel NL
	Coefficient	length	coefficient
$(k, \varphi, \theta)^*$	ijk	$\pm l_{lik}(m\mu)$	$\pm d_{ijk}(\sigma)^{\dagger}$
b,0,0	333	7.5	0.40 (8)
b,0,90	311	2.5	0.14(1)
b,90,45	113	33	0.11(1)
a,0,90	322	4.2	0.15 (8)
a,90,45	223	18	0.007 (4)

\* k = propagation direction,  $\theta = \text{angle}$  between the pump (1.06 $\mu$ ) polarization and the c axis,  $\varphi = \text{angle}$  between the harmonic (0.53 $\mu$ ) polarization and the c axis.

† Estimated standard deviation ( $\sigma$ ) represents the variation in the last figure, also  $d_{311}d_{333} < 0$ .

Once the coherence lengths and indices at 0.53  $\mu$ m (Table 4) are known, one can calculate the indices at 1.06  $\mu$ m using

$$l_{ijk} = \frac{1 \cdot 0 \ \mu \text{m}}{4[n_i - \frac{1}{2}(n_j + n_k)]} \tag{5}$$

where the subscript *i* refers to the electric field polarization direction (a, b, c < = >x, y, z < = >1, 2, 3) at the harmonic  $(0.53 \ \mu\text{m})$ , *j* and *k* the polarization directions at the fundamental  $(1.06 \ \mu\text{m})$ . The calculated indices at  $1.06 \ \mu\text{m}$  are also listed in Table 5.

Since the laser power  $[P(\omega) \sim 100 \text{ MW}]$ , mode structure and focused spot size  $(\sim 25\mu)$  are constant from

one measurement to the next, the relative external SH power  $P(2\omega)$  from material A and material B is related [Wynne & Bloembergen (1969)] to the nonlinear coefficients (d's), the coherence lengths (l's) and indices n by



Fig. 1. (a) Projection down c on  $Ca(IO_3)_2.6H_2O$ . Only a unit  $\frac{1}{2}$  along a and b of the face-centered lattice is shown. The calcium ions are located on twofold axes and are surrounded by eight oxygen atoms in a pseudo-Archimedian antiprism. (b) Projection down a. Only the contents of the cell between x = 0.0 and x = 0.5 are shown. The trigonal pyramidal iodate ions are primarily pointing along the a, not c, direction.



Fig. 2. Block diagram of experimental setup used to measure SHG in  $Ca(IO_3)_2$   $.6H_2O$ .

where  $n_{1,4}$  and  $n_{2,4}$  refer to the indices at the fundamental and harmonic respectively.

The linear Fresnel power reflection coefficient is

$$R^{F} = \frac{(n-1)^{2}}{(n+1)^{2}} \,. \tag{7}$$

In our particular experimental setup we immerse the crystal in an oil of index n=1.5 to decrease reflection losses, hence

$$R^{F} = \frac{(n-1\cdot 5)^{2}}{(n+1\cdot 5)^{2}}.$$
 (8)

Corrections for losses due to absorption and finite beam width compared to fringe spacing, discussed in detail by Boyd, Kasper & McFee (1971), were considered negligible ( $\sim 2\%$  or less) in this particular case. Experimental results are summarized in Table 5.



Fig. 3. (a) Ca(IO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O wedge configuration used for coupling to  $d_{33}$ ,  $d_{31}$ ,  $d_{15}$ . Propagation direction corresponds to k along the y axis

Coefficient	Fundamental polarization	Harmonic polarization	
<i>d</i> <sub>33</sub>	$E_z$	$E_z$	
$d_{31} \\ d_{15}$	$45^{\circ}$ to Z	$E_z E_x$	

(b)  $Ca(IO_3)_2$ .  $6H_2O$  wedge configuration used for coupling to  $d_{33}$ ,  $d_{32}$ ,  $d_{24}$ . Propagation direction corresponds to k along the x axis.

e n unisi	Fundamental	Harmonic
Coefficient	polarization	polarization
$d_{33}$	$E_z$	$E_z$
$d_{32}$	$E_y$	$E_z$
$d_{24}$	45° to Z	$E_y$

The sign of  $d_{311}$  was found to be opposite to that of  $d_{333}$  while their respective coherence lengths were observed to have the same signs, as determined by interference methods (Miller, Nordland, Kolb & Bond, 1970; Crane, 1972). We were unable to determine the relative sign of  $d_{322}$  since its small magnitude precluded the observation of interference between it and  $d_{333}$ .

#### (b) Discussion

It is unfortunate, from a device point of view, that the largest coefficient  $(d_{333})$  is not phase-matchable. Since the larger of the remaining coefficients  $(d_{311})$  is approximately a tenth the size of  $d_{311}$  of LiIO<sub>3</sub> the material shows little promise as a frequency doubler for 1.06  $\mu$ m.

Considering the accuracy with which the nonlinear coefficients were measured, the Kleinman (1962) symmetry conditions are obeyed, *i.e.*  $(d_{311} = d_{113}, d_{322} = d_{223})$ .

Using the model of Jeggo & Boyd (1970) we have formulated the nonlinearities in terms of a distorted octahedron of oxygens about the iodine atom. This technique has recently been applied by Jeggo (1970) to HIO<sub>3</sub> and LiIO<sub>3</sub> using the Miller (1964) reduced tensor  $\delta_{ijk}$  rather than the measured  $d_{ijk}$ 's, where

$$\delta_{ijk} = \frac{d_{ijk}}{\chi_i \chi_j \chi_k} \,. \tag{9}$$

Since the Kleinman symmetry condition is implicit in the bond model our observed  $\delta$ 's ( $\delta_{311}^c$  and  $\delta_{322}^c$ ) shown in Table 6 are calculated from the average d's (Table 5). The equations relating the  $\delta$ 's to the microscopic nonlinear bond polarizabilities ( $\beta$ 's) for the 3 iodate crystals [LiIO<sub>3</sub>, HIO<sub>3</sub>, Ca(IO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O labeled with superscripts L, H and C, respectively] are

$$\delta_{333}^{\rm L} V^{\rm L} = \sum n_i^3 \beta_i = 0.656 \ \beta_1 - 1.267 \ \beta_2 \tag{10}$$

$$\delta_{311}^{\rm L} V^{\rm L} = \sum n_i l_i^2 \beta_i = 1.107 \ \beta_1 - 1.152 \ \beta_2 \tag{11}$$

$$\delta_{233}^{\rm H} V^{\rm H} = \sum l_i m_i n_i \beta_i = -1.169 \ \beta_1 + 1.384 \ \beta_2 \quad (12)$$

$$\delta_{333}^{\rm C} V^{\rm C} = \sum n_i^3 \beta_i = -12.37 \ \beta_1 + 12.08 \ \beta_2 \tag{13}$$

$$\delta_{311}^{\rm C} V^{\rm C} = \sum n_i l_i^2 \beta_i = 3.23 \ \beta_1 - 2.53 \ \beta_2 \tag{14}$$

$$\delta_{322}^{\rm C} V^{\rm C} = \sum n_i m_i^2 \beta_i = 1.46 \ \beta_1 - 0.48 \ \beta_2 \tag{15}$$

where  $\beta_1$  and  $\beta_2$  represent the nonlinear bond polarizabilities of the short (~1.8 Å) and long (~2.8 Å) iodine-oxygen bonds respectively. The *i*th bond has direction cosines  $l_im_in_i$  (from I to O) and sums are taken over the unit cell of volume V. The respective volumes ( $V^L$ ,  $V^H$ ,  $V^C$ ) are (1.345, 2.522, 21.74) × 10<sup>-28</sup> m<sup>3</sup>. Using equations (10), (11), (12) and the sign relationships found by Jeggo ( $\delta_{333}^L \delta_{123}^H < 0$ ) and Jerphagnon (1970) ( $\delta_{333}^L \delta_{311}^L > 0$ ), we find  $\beta_1 = 1.57 \times 10^{-28}$  m<sup>3</sup> and  $\beta_2 = 2.47 \times 10^{-28}$  m<sup>3</sup>. Substituting these  $\beta$ 's into equations (13), (14), (15) we then determine that  $\delta_{333}^C \delta_{333}^L < 0$ ,  $\delta_{333}^C \delta_{311}^L < 0$  (also determined experimentally) and  $\delta_{333}^2 \delta_{322}^2 > 0$ . Using these sign assignments we find a best least-squares fit for the observed and calculated  $\delta$ 's (Table 6) is obtained for  $\beta_1 = 1.13 \times 10^{-28}$  m<sup>3</sup> and  $\beta_2 = 2.24 \times 10^{-28}$  m<sup>3</sup>. The agreement (average error ~25%) is within the experimental uncertainties. The absolute magnitudes of  $\beta_1$  and  $\beta_2$  are respectively  $0.72 \times 10^{-40}$  m<sup>4</sup>/V and  $1.43 \times 10^{-40}$  m<sup>4</sup>/V [using  $d_{123}$ (KH<sub>2</sub>PO<sub>4</sub>) =  $0.628 \times 10^{-12}$  m/V], which is of the order of that found in other materials such as LiNbO<sub>3</sub>, LiTaO<sub>3</sub>, *etc.* (Jeggo, 1970). Furthermore, the ratio ( $\beta_2/\beta_1$ )<sub>obs</sub> = 2.0 is in agreement with the recent theoretical result of Levine (1973), which states that  $\beta$  should increase approximately as the square of the bond length, *i.e.* ( $\beta_1/\beta_2$ )<sub>calc</sub> = (2.8/1.8)<sup>2</sup> = 2.4. Future experiments can hopefully determine whether indeed  $\delta_{333}^{L3}\delta_{123}^{H} < 0$  and  $\delta_{333}^{L3}\delta_{333}^{c} < 0$ , as predicted by the model.

# Table 6. Observed and calculated Miller deltas $(\delta_{iik})$

 $\delta$ (calc) were obtained from nonlinear bond polarizabilities,  $\beta_1$ and  $\beta_2$  (see text).  $\delta$ (obs) were obtained from  $d_{333}$ (LiIO<sub>3</sub>) =  $\pm 12.4 \ d_{123}$ (KH<sub>2</sub>PO<sub>4</sub>),  $d_{311}$ (LiIO<sub>3</sub>) =  $\pm 11.9 \ d_{123}$ (KH<sub>2</sub>PO<sub>4</sub>), Jerphagnon[(1970),  $d_{123}$ (HIO<sub>3</sub>) =  $\pm 10.2 \ d_{123}$  (KH<sub>2</sub>PO<sub>4</sub>), Bjorkholm (1968), and Table 5; hence all  $\delta$  are relative to  $d_{123}$ (KH<sub>2</sub>PO<sub>4</sub>).

Compound	$\delta_{ijk}$	$ \delta $ (obs)	$\delta(calc)$
HIO3	$\delta_{123}^{H}$	0.55	+0.70
$Ca(IO_3)_2 \cdot 6H_2O$	$\delta_{333}^{C}$	0.87	+0.60
$Ca(IO_3)_2 \cdot 6H_2O$	$\delta_{311}^{c}$	0.39	-0.09
$Ca(IO_3)_2.6H_2O$	$\delta^{\rm C}_{322}$	0.03	+0.03
LiIO <sub>3</sub>	$\delta^{L}_{333}$	1.57	-1.56
LiIO <sub>3</sub>	$\delta^{L}_{311}$	0.96	-0.98

In view of this relationship between nonlinear susceptibility and bond length one should search for nonlinear materials where the bonded interactions are just less than a van der Waals length. This point might be further clarified by studying the newly discovered ferroelectric MTeO<sub>3</sub> (M = Ca, Sr, Ba, etc.) compounds (Yamada & Iwasaki, 1972) which are isostructural with the iodates in the sense that like the MIO<sub>3</sub> (M =H, Li, Na, *etc.*) compounds, they will also contain a severely distorted oxygen octahedron about the Te atom due to the Te nonbonded pair. With more optical data on these isoelectronic systems one might also learn the degree to which the lone pair itself contributes to the nonlinear polarizability, an as yet completely unknown quantity.

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