Acta Cryst. (1973). B29, 1067

Crystal Structure, Linear and Nonlinear Optical Properties of $Ca(IO_3)_2.6H_2O$*

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.*

(*Received* 19 *October* 1972; *accepted* 29 *January* 1973)

The room-temperature crystal structure of $Ca(IO_3)_2.6H_2O$ 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 *Fdd*2 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 0.53μ 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} ($LiIO_3$) are respectively 0·14, 0·015, 0·40, 0·11, 0·007. The nonlinear bond polarizability β for the long (~ 2.8 Å) I–O bond is found to be twice that of the short (~ 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 $Ca(IO_3)_2.6H_2O$ 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 $LiIO_3$ and HIO_3 (Jeggo, 1970) showed that, of the two sets of iodine–oxygen bonds, the longer set (I–O ~ 2.8 Å, essentially a van der Waals interaction) contributes twice as much to the optical nonlinearity as does the shorter set (I–O ~ 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.

* Work supported in part by the U.S. Atomic Energy Commission.

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 *Fdd*2 was established on the basis of systematic extinctions ($h+k$, $k+l$ and hence $l+h$ odd for hkl, $k+l\neq 4n$ for $0kl$, and $h+l\neq 4n$ for $h0l$ reflections 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 $Ca(IO_3)_2.6H_2O$ per cell, the calculated density is 3·05 g cm^{-3}. (BLPT reports 2·97 g cm^{-3} 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 θ–2θ scan technique was used with a scan speed of $\frac{1}{2}$ deg min^{-1} over the interval $2\theta_{\lambda_1}-0{\cdot}80°$ to $2\theta_{\lambda_2}+0{\cdot}80°$. Of these data, 23 were measured to be less than 3σ, where $\sigma=\surd(N_{SC}+K^2 . N_B)$ in which N_{SC}, N_B, 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 3σ and considered to be unobserved in subsequent calculations.

Absorption corrections ($\mu_{Mo\ K\alpha}=63{\cdot}4\ cm^{-1}$) 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 × 0·34 × 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^{2+} 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 *Fdd*2, 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 $(0,0,z$ and $\frac{1}{4},\frac{1}{4},\frac{3}{4}+z)$ 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 $\mathscr{R}$ index ratio is $\mathscr{R}=0{\cdot}049/0{\cdot}047=1{\cdot}04$; 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 ($\pm l$) of reflections for which the structure factor with and without dispersion resulted in a 5% difference. The entire data set (except 040 which was considered to suffer secondary extinction) were subjected to least-squares refinement with anisotropic thermal parameters yielding $R=0{\cdot}032$; parameters obtained are listed in Table 1.* The average dispersion corrected observed structure factors are compared with the calculated values in Table 2.

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

(*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

* After this paper was accepted, the authors had a discussion with S. C. Abrahams concerning the possibility of achieving either (*a*) an $\mathscr{R}$ 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, $+l$) 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 $\mathscr{R}$ index ratio ($0{\cdot}031/0{\cdot}036=1{\cdot}14$) 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 ($+l$) 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 $0{\cdot}3\times\sigma$.

Table 1. *Positional and thermal parameters for* $Ca(IO_3)_2.6H_2O$

Anisotropic thermal parameters are of the form $\exp\left[-\left(\frac{1}{4}\sum_{i}^{3}\sum_{j}^{3}B_{ij}a_i^*a_j^*h_ih_j\right)\right]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	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)	2·1 (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)

Table 2. *Average observed and calculated structure factors*

K	10FO	10FC	K	10FO	10FC	K	10FO	10FC	K	10FO	10FC	K	10FO	10FC	K	10FO	10FC	K	10FO	10FC	K	10FO	10FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

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°)

Separations (Å)		Bond angles (°)	
Ca--O(2)	2·47	O(2)–Ca–O(2′)	78·2
Ca--O(4)	2·52	O(4)–Ca–O(4′)	152·7
Ca--O(5)	2·44	O(5)–Ca–O(5′)	152·3
Ca--O(6)	2·50	O(6)–Ca–O(6′)	74·7
		O(4)–Ca–O(6)	69·2
O(4)–O(5)	2·92	O(2)–Ca–O(5)	71·2
		O(4)–Ca–O(5)	72·1
O(4)–O(6)	2·85	O(2)–Ca–O(4)	72·4
O(4)–O(2)	2·94	O(5)–Ca–O(6)	78·7
O(5)–O(6)	3·15	O(5)–Ca–O(6)	79·4
O(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 (e.s.d. O–O, 0·03 Å; O–O–O, 0·9°)

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)	76·2
		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)	2·87	O(2)–O(6)–O(4)	173·1
O(6)–O(4)	2·85	O(1)–O(6)–O(4)	100·4
O(6)–O(1)	2·93	O(2)–O(6)–O(1)	85·8

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 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

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 0·53μ, as determined from index matching oils and birefringence measurements, are given in Table 4. It is seen that $Ca(IO_3)_2.6H_2O$ is negative biaxial. The twofold polar axis is z, the acute bisectrix x, and the obtuse bisectrix z.

Table 4. *Refractive indices of* $Ca(IO_3)_2.6H_2O$

Refractive index	At 0·53μ	At 1·06μ
n_x	1·625	1·582
n_y	1·654	1·625
n_z	1·688	1·653

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

$$\begin{bmatrix} 0 & 0 & 0 & 0 & d_{113} & 0 \\ 0 & 0 & 0 & d_{223} & 0 & 0 \\ d_{311} & d_{322} & d_{333} & 0 & 0 & 0 \end{bmatrix}.$$

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

$$P_x = 2d_{113}E_xE_z \tag{1}$$

$$P_y = 2d_{223}E_yE_z \tag{2}$$

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

The coefficients were measured relative to d_{333} of $LiIO_3$ by SHG experiments using a Q switched Nd-YAG laser operating at $1{\cdot}06\mu$. The experimental setup is shown in Fig. 2. Samples were prepared in the form of thin wedges ($\sim 5\times 2$ mm, $\theta = 3{\cdot}5°$), 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 (θ) by

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

Observed coherence lengths are given in Table 5.

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

(k,φ,θ)*	Coefficient ijk	Coherence length $\pm l_{ijk}$(mμ)	Rel NL coefficient $\pm d_{ijk}(\sigma)$†
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, θ = angle between the pump ($1{\cdot}06\mu$) polarization and the c axis, φ = angle between the harmonic ($0{\cdot}53\mu$) polarization and the c axis.

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

Once the coherence lengths and indices at $0{\cdot}53\ \mu$m (Table 4) are known, one can calculate the indices at $1{\cdot}06\ \mu$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 ($0{\cdot}53\ \mu$m), j and k the polarization directions at the fundamental ($1{\cdot}06\ \mu$m). The calculated indices at $1{\cdot}06\ \mu$m are also listed in Table 5.

Since the laser power [$P(\omega) \sim 100$ 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

$$\frac{P_B}{P_A} = \left[\frac{l_B}{l_A}\right]^2 \left[\frac{d_B}{d_A}\right]^2 \left[\frac{n_{1A}^2 n_{2A}}{n_{1B}^2 n_{2B}}\right] \left[\frac{(1-R_{1B}^F)^2(1-R_{2B}^F)}{(1-R_{1A}^F)^2(1-R_{2A}^F)}\right], \tag{6}$$

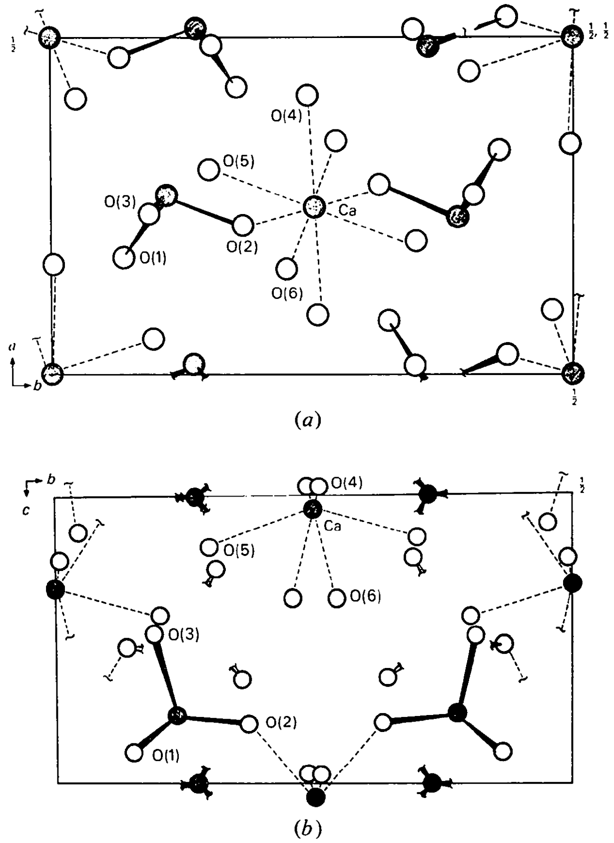


Fig. 1. (*a*) Projection down **c** on $Ca(IO_3)_2.6H_2O$. Only a unit $\frac{1}{2}$ along **a** and **b** of the face-centered lattice is shown. The calcium ions are located on twofold axes and are surrounded by eight oxygen atoms in a pseudo-Archimedian antiprism. (*b*) Projection down **a**. Only the contents of the cell between $x = 0{\cdot}0$ and $x = 0{\cdot}5$ are shown. The trigonal pyramidal iodate ions are primarily pointing along the **a**, not **c**, direction.

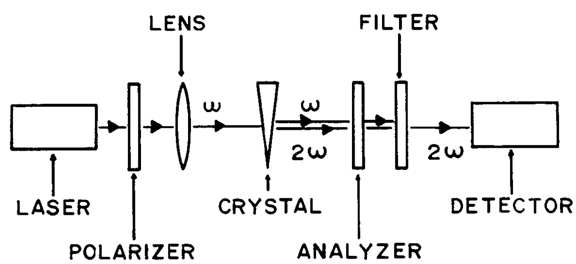


Fig. 2. Block diagram of experimental setup used to measure SHG in $Ca(IO_3)_2.6H_2O$.

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

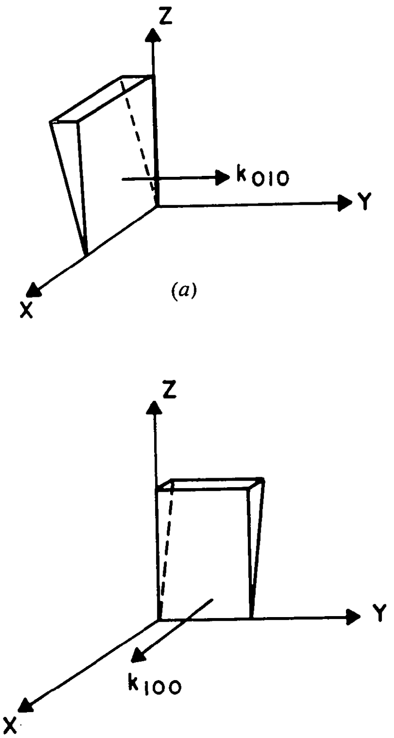
The linear Fresnel power reflection coefficient is

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

In our particular experimental setup we immerse the crystal in an oil of index $n=1{\cdot}5$ to decrease reflection losses, hence

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

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.



(a)

(b)

Fig. 3. (a) $Ca(IO_3)_2.6H_2O$ 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
d_{33}	E_z	E_z
d_{31}	E_x	E_z
d_{15}	45° to 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.

Coefficient	Fundamental polarization	Harmonic 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 $LiIO_3$ the material shows little promise as a frequency doubler for 1·06 μm.

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_3 and $LiIO_3$ using the Miller (1964) reduced tensor δ_{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 δ's ($\delta^{\mathrm{C}}_{311}$ and $\delta^{\mathrm{C}}_{322}$) shown in Table 6 are calculated from the average d's (Table 5). The equations relating the δ's to the microscopic nonlinear bond polarizabilities (β's) for the 3 iodate crystals [$LiIO_3$, HIO_3, $Ca(IO_3)_2.6H_2O$ labeled with superscripts L, H and C, respectively] are

$$\delta^{\mathrm{L}}_{333}V^{\mathrm{L}} = \sum n_i^3\beta_i = 0{\cdot}656\ \beta_1 - 1{\cdot}267\ \beta_2 \tag{10}$$

$$\delta^{\mathrm{L}}_{311}V^{\mathrm{L}} = \sum n_i l_i^2\beta_i = 1{\cdot}107\ \beta_1 - 1{\cdot}152\ \beta_2 \tag{11}$$

$$\delta^{\mathrm{H}}_{233}V^{\mathrm{H}} = \sum l_i m_i n_i \beta_i = -1{\cdot}169\ \beta_1 + 1{\cdot}384\ \beta_2 \tag{12}$$

$$\delta^{\mathrm{C}}_{333}V^{\mathrm{C}} = \sum n_i^3\beta_i = -12{\cdot}37\ \beta_1 + 12{\cdot}08\ \beta_2 \tag{13}$$

$$\delta^{\mathrm{C}}_{311}V^{\mathrm{C}} = \sum n_i l_i^2\beta_i = 3{\cdot}23\ \beta_1 - 2{\cdot}53\ \beta_2 \tag{14}$$

$$\delta^{\mathrm{C}}_{322}V^{\mathrm{C}} = \sum n_i m_i^2\beta_i = 1{\cdot}46\ \beta_1 - 0{\cdot}48\ \beta_2 \tag{15}$$

where β_1 and β_2 represent the nonlinear bond polarizabilities of the short ($\sim 1{\cdot}8$ Å) and long ($\sim 2{\cdot}8$ Å) iodine–oxygen bonds respectively. The ith bond has direction cosines $l_i m_i n_i$ (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) $\times 10^{-28}$ m^3. Using equations (10), (11), (12) and the sign relationships found by Jeggo ($\delta^{\mathrm{L}}_{333}\delta^{\mathrm{H}}_{123}<0$) and Jerphagnon (1970) ($\delta^{\mathrm{L}}_{333}\delta^{\mathrm{L}}_{311}>0$), we find $\beta_1 = 1{\cdot}57\times 10^{-28}$ m^3 and $\beta_2 = 2{\cdot}47\times 10^{-28}$ m^3. Substituting these β's into equations (13), (14), (15) we then determine that $\delta^{\mathrm{C}}_{333}\delta^{\mathrm{L}}_{333}<0$, $\delta^{\mathrm{C}}_{333}\delta^{\mathrm{C}}_{311}<0$ (also determined experimentally) and $\delta^{\mathrm{C}}_{333}\delta^{\mathrm{C}}_{322}>0$. Using these sign assignments we find a best least-squares fit for the observed and calculated δ's (Table 6) is obtained for $\beta_1 = 1{\cdot}13\times 10^{-28}$ m^3 and

$\beta_2 = 2{\cdot}24 \times 10^{-28}$ m^3. The agreement (average error $\sim$25%) is within the experimental uncertainties. The absolute magnitudes of β_1 and β_2 are respectively $0{\cdot}72 \times 10^{-40}$ m$^4/V$ and $1{\cdot}43 \times 10^{-40}$ m$^4/V$ [using $d_{123}(KH_2PO_4) = 0{\cdot}628 \times 10^{-12}$ m/V], which is of the order of that found in other materials such as $LiNbO_3$, $LiTaO_3$, *etc.* (Jeggo, 1970). Furthermore, the ratio $(\beta_2/\beta_1)_{obs} = 2{\cdot}0$ is in agreement with the recent theoretical result of Levine (1973), which states that β should increase approximately as the square of the bond length, *i.e.* $(\beta_1/\beta_2)_{calc} = (2{\cdot}8/1{\cdot}8)^2 = 2{\cdot}4$. Future experiments can hopefully determine whether indeed $\delta^L_{333}\delta^H_{123} < 0$ and $\delta^L_{333}\delta^c_{333} < 0$, as predicted by the model.

Table 6. *Observed and calculated Miller deltas* (δ_{ijk})

δ(calc) were obtained from nonlinear bond polarizabilities, β_1 and β_2 (see text). δ(obs) were obtained from $d_{333}(LiIO_3) = \pm 12{\cdot}4$ $d_{123}(KH_2PO_4)$, $d_{311}(LiIO_3) = +11{\cdot}9$ $d_{123}(KH_2PO_4)$, Jerphagnon (1970), $d_{123}(HIO_3) = \pm 10{\cdot}2$ d_{123} (KH_2PO_4), Bjorkholm (1968), and Table 5; hence all δ are relative to $d_{123}(KH_2PO_4)$.

Compound	δ_{ijk}	$\lvert\delta\rvert$(obs)	δ(calc)
HIO_3	δ^H_{123}	0·55	+0·70
$Ca(IO_3)_2 \cdot 6H_2O$	δ^C_{333}	0·87	+0·60
$Ca(IO_3)_2.6H_2O$	δ^C_{311}	0·39	−0·09
$Ca(IO_3)_2.6H_2O$	δ^C_{322}	0·03	+0·03
$LiIO_3$	δ^L_{333}	1·57	−1·56
$LiIO_3$	δ^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 $MTeO_3$ (M = Ca, Sr, Ba, *etc.*) compounds (Yamada & Iwasaki, 1972) which are isostructural with the iodates in the sense that like the MIO_3 (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.

References

Bergman, J. G. Boyd, G. D., Ashkin, A. & Kurtz, S. K. (1969). *J. Appl. Phys.* **40**, 2860–2863.

Bergman, J. G. & Kurtz, S. K. (1970). *Mater. Sci. Eng.* **5**, 235–250.

Bjorkholm, J. E. (1968). *IEEE J. Quantum Electron.* QE–**4**, 970–972.

Boyd, G. D., Kasper, H. & McFee, J. H. (1971). *IEEE J. Quantum Electron.* QE–7, 563–573.

Braibanti, A., Lanfredi, A. M., Pellinghelli, M. A. & Tiripicchio, A. (1971). *Inorg. Chim Acta*, **5**, 590–594.

Cingi, M. B., Emiliani, F. & Gusatini, C. (1967). *Acta Cryst.* **23**, 1114.

Crane, G. R. (1973). *J. Appl. Phys.* **44**, 915–916.

Donnay, J. D. H. (1943). *Amer. Min.* **28**, 313–328.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Hulme, K. F. (1973). *Rep. Prog. Phys.* To be published.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Jeggo, C. R. (1970). *Optics Commun.* **1**, 375–376.

Jeggo, C. R. & Boyd, G. D. (1970). *J. Appl. Phys.* **41**, 2741–2743.

Jerphagnon, J. (1970). *Appl. Phys. Lett.* **16**, 298–299.

Keve, E. T., Abrahams, S. C. & Bernstein, J. L. (1971). *J. Chem. Phys.* **54**, 2556–2563.

Kleinman, D. A. (1962). *Phys. Rev.* **126**, 1977–1979.

Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3813.

Kurtz, S. K., Perry, T. T. & Bergman, J. G. (1968). *Appl. Phys. Lett.* **12**, 186–188.

Levine, B. F. (1973). *Phys. Rev.* To be published.

Miller, R. C. (1964). *Appl. Phys. Lett.* **5**, 17–19.

Miller, R. C., Nordland, W. A., Kolb, E. D. & Bond, W. L. (1970). *J. Appl. Phys.* **41**, 3008–3011.

Morosin, B. (1967). *Acta Cryst.* **23**, 630–634.

Nye, J. F. (1964). *Physical Properties of Crystals.* New York: Oxford Press.

Templeton, D. H. (1955). *Acta Cryst.* **8**, 842.

Wynne, J. J. & Bloembergen, N. (1969). *Phys. Rev.* **188**, 1211–1220.

Yamada, T. & Iwasaki, H. (1972). *Appl. Phys. Lett.* **21**, 89–90.