# A Powder Technique for the Evaluation of Nonlinear Optical Materials 

S. K. Kurtz and T. T. Perry<br>Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

(Received 15 January 1968; in final form 8 March 1968)


#### Abstract

An experimental technique using powders is described which permits the rapid classification of materials according to (a) magnitude of nonlinear optical coefficients relative to a crystalline quartz standard and (b) existence or absence of phase matching direction(s) for second-harmonic generation.

Results are presented for a large number of inorganic and organic substances including single-crystal data on phase-matched second-harmonic generation in $\mathrm{HIO}_{3}, \mathrm{KNbO}_{3}, \mathrm{PbTiO}_{3}, \mathrm{LiClO}_{4} \cdot 3 \mathrm{H}_{2} \mathrm{O}$, and $\mathrm{CO}\left(\mathrm{NH}_{2}\right)_{2}$. Iodic acid ( $\mathrm{HIO}_{3}$ ) has a nonlinear coefficient $d_{14} \sim 1.5 \times d_{31} \mathrm{LiNbO}_{3}$. Since it is readily grown from water solution and does not exhibit optical damage effects, this material should be useful for nonlinear device applications.


## I. INTRODUCTION

Much current interest in quantum electronics has centered on finding materials which have suitable nonlinear optical properties for use as the active media in (1) efficient second harmonic generators, ${ }^{1}$ (2) tunable parametric oscillators, ${ }^{2}$ and (3) broadband electrooptic modulators. ${ }^{3}$

While no single set of criteria for the selection of such materials can be laid down which apply to all three of these applications, one can utilize recent theories ${ }^{4}$ to predict ${ }^{5}$ the magnitude of the nonlinear optical coefficients of a wide variety of substances. Recent measurements ${ }^{6}$ have demonstrated the usefulness of these predictions, but the presently available experimental methods require single crystals of reasonably good optical and dielectric quality. Single crystals meeting these requirements are difficult to obtain since in most cases a substantial and costly materials growth program must be undertaken for each individual material.

In this article we describe a simple and quick experimental technique which only requires the material in powder form (which is readily available in most cases). While previous workers ${ }^{7}$ have reported detecting second-

[^0]harmonic generation in crystalline powders, the present study is to the author's knowledge the first systematic investigation of this effect. With a reasonably high reliability the method enables one to classify a new material in one of five categories:

Class A: phase-matchable for second-harmonic generation; nonlinear coefficients large (substantially greater than crystalline quartz),

Class B: phase-matchable for second-harmonic generation; nonlinear coefficients small (same order of magnitude as crystalline quartz),

Class C: nonlinear coefficients greater than crystalline quartz; not phase-matchable for second-harmonic generation,

Class D: nonlinear coefficients equal to or less than crystalline quartz; not phase-matchable for secondharmonic generation,

Class E: centrosymmetric (first-order nonlinearities vanish due to symmetry considerations).

The paper is divided into the following headings. Section II describes the experimental apparatus. In Sec. III experimental results are described for materials having known nonlinear coefficients. Section IV describes a theory which accounts at least in part for the results of Sec. III. Section V reports the results of a survey of a large number of new materials. In Sec. VI results for the nonlinear coefficients (and phasematching properties) of several single crystals of new nonlinear optical materials are presented which confirm the predictions of the powder method. Finally in Sec. VII we conclude with a summary of the powder method.

## II. EXPERIMENTAL APPARATUS AND TECHNIQUE

## A. Basic Configuration for Powder SHG

The basic configuration used for the study of secondharmonic generation in powders is shown in Fig. 1. It consists of a $Q$-switched laser whose beam falls unfocused onto a thin section $(\sim 0.2 \mathrm{~mm})$ of powder of the material under study. After the fundamental beam is removed by a series of short wavelength passing filters, the second
harmonic is detected by a photomultiplier and displayed on an oscilloscope. A reference beam is obtained by use of beam splitter placed ahead of the sample. This enables the intensity of the fundamental or second harmonic generated in a reference sample ${ }^{8}$ (including variations in the intensities and mode structure of successive pulses) to be monitored by displaying both signals simultaneously on a dual-beam scope. The system also permitted the insertion of narrow-pass filters at the second-harmonic wavelength between the Shott filters and the photomultiplier to eliminate spurious signals (such as those due to multiple-photon absorption). In order to improve the efficiency of secondharmonic collection at the detector, a parabolic reflector was placed directly in front of the sample (i.e., between the laser and the sample) with a small access hole for the laser beam. In certain cases described in the next section this reflector was replaced with an integrating sphere, the sample being mounted at the center of the sphere. For most of the work a $\mathrm{Nd}: \mathrm{CaWO}_{4}$ laser was used having peak pulse powers in the vicinity of 100 W and pulsewidths of $200 \mu \mathrm{sec}$ (i.e., 0.02 J ). The repetition rate for this laser was limited to a maximum of one shot every 30 sec . The beam diameter at the sample was $\sim 5 \mathrm{~mm}$. A Nd:YAG laser was also used. It was $Q$ switched by a rotating mirror at a rate of 400 Hz . Peak powers in this case were $\sim 1 \mathrm{~kW}$ with pulsewidths of $\sim 200 \mathrm{nsec}$.

## B. Sample Preparation and Mounting

Samples were prepared and mounted using several techniques. For qualitative results and for most initial survey work a thin layer ( $\sim 0.2 \mathrm{~mm}$ ) of ungraded powder was placed on a microscope slide and held in place with transparent tape. For quantitative work, powders were graded by use of standard sieves to the desired range of particle sizes (usually $75-150 \mu$ ) and loaded into a quartz cell of known thickness ( 0.2 mm , 1 mm , etc.) with the aid of a vibrator to assure uniform


Fig. 1. Apparatus used for study of second-harmonic generation in powders.

[^1]packing. Particle sizes were checked by standard optical microscopy techniques. In the case of materials such as quartz, zinc oxide, and other materials having known nonlinear coefficients and available in singlecrystal form, powders were made from single crystals using a Spex vibrating ball mill, and then graded using standard sieves. A similar procedure was followed in the case of minerals of polycrystalline or single-crystalline character.

## C. Single-Crystal SHG Apparatus

A block diagram of the apparatus being used for single-crystal SHG measurements is shown in Fig. 2. This system is an improved version of one developed by Smith ${ }^{9}$ for second-harmonic generation studies. This system differs from previous systems in that continuous recording of second-harmonic intensity as a function of angle, temperature, or other variables is possible even in crystals having nonlinear coefficients two orders of magnitude or more smaller than quartz. It thus permits a rapid and accurate measurement of the nonlinear coefficients and phase-matching properties of new materials, thereby providing both a verification of the powder SHG results and a more detailed description of the nonlinear optical properties once single crystals of a new material become available.

## III. EXPERIMENTAL RESULTS

In order to determine the essential features of secondharmonic generation in thin powder layers, a series of experiments were performed to measure the dependence of second-harmonic intensity on the following parameters (see Fig. 3): (1) angle between detector and direction of incident light beam ( $\equiv \theta$ ), (2) powder-layer thickness ( $\equiv L$ ), (3) average particle size ( $\equiv \hat{r}$ ), and (4) laser-beam diameter $(\equiv D)$.

Within certain ranges of layer thickness and particle size it was found that a fairly simple and reproducible dependence on each of the above parameters could be obtained. The following discussion is limited to this domain. Basically the region is one in which $\hat{\gamma} \ll L \ll D$. This ordering insures that the fundamental beam strikes a large number particles of random orientation, thereby performing a significant statistical average. In addition a planar geometry is retained. Taken together these factors result in a considerable simplification of the theoretical analysis which is given in the next section.

## A. Angular Distribution

When the average particle size, layer thickness, and beam diameter satisfy the inequality given above, it is found that the angular distribution of second-harmonic intensity for the powder in air is nearly cosinusoidal in $\theta$ for both the forward and backward scattering directions.

[^2]

Fig. 2. Experimental configuration used for single-crystal measurements.

Thus, the sample considered as a source of secondharmonic radiation behaves like an isotropic planar radiator obeying Lambert's (cos) law ${ }^{10}$

$$
I(\theta, \Phi)=I_{o} \cos \theta
$$

where $\theta$ and $\Phi$ are spherical polar angles and the photometric intensity $I_{o}($ energy $/ \mathrm{sec} / \mathrm{sr})$ is defined as

$$
I_{o} \equiv \int B d S
$$

where $B$ is the photometric brightness and $d S$ is a surface element. A typical measured angular dependence is illustrated in Fig. 3. The photometric intensity $I_{o}$ of the front and back surfaces of the powder layer is not in general equal for powders in air. As the particle size decreases, the second-harmonic lobe in backward direction grows while that in the forward direction diminishes (relative to the situation where they are equal). Thus, sampling of the harmonic intensity in the forward direction alone can give misleading results if the backward lobe is not taken into account. An integrating Ulbicht sphere ${ }^{11}$ can be used in this case to

[^3]obtain readings proportional to the total integrated harmonic flux. As we shall see, however, the powder second-harmonic intensities for non-phase-matchable materials are low. Combined with the relatively low efficiency of the integrating sphere, this leads to detection problems unless the fundamental power densities are quite high. When the particle size $r$ approaches the layer thickness $L$ appreciable deviations from the cos distribution are observed, particularly for phase- matchable materials.
Also indicated in Fig. 3 is the intensity distribution when the same powder is contained in a liquid of matching refractive index. (In the case of ADP shown here, which is uniaxial, the index of the liquid was chosen to approximately match the average of the ordinary and extraordinary indices, i.e., $n_{1 \mathrm{iq}}=1.51$.) The advantage of the index matching of the powder is evident in that the second harmonic is not significantly scattered due to reflection and refraction at particle interfaces, and hence all the harmonic flux is contained in a narrow cone in the forward direction.

## B. Dependence of $I^{2 \omega}$ on Layer Thickness $L$

The second-harmonic signal was found to vary linearly with layer thickness $L$ for fixed particle size $r$ after integrating over the $4 \pi$ solid angle. This implies


Fig. 3. Angular distribution of second harmonic generated in ADP powders.
that the second-harmonic intensity is proportional to the total number of particles present. A linear dependence on $L$ was also found in the case of immersion of the powder in an index-matching liquid.

## C. Dependence of $I^{2 \omega}$ on Average Particle Size $\hat{r}$

Keeping the layer thickness $L$ fixed, the variation of $I^{2 \omega}$ (integrated over $4 \pi$ solid angle) with average particle size $\hat{r}$ is shown in Fig. 4 for ZnO which is not phase-matchable. ${ }^{12}$ The interpretation of this curve is discussed in the next section along with the theory. The important features of the particle-size dependence


Fig. 4. Particle-size dependence of second-harmonic intensity for zinc oxide powders in integrating sphere.

[^4]

Fig. 5. Particle-size dependence of second-harmonic intensity from quartz powders in index-matching liquid.
illustrated in Fig. 4 are: (1) a peak in the intensity when the particle size is close to the average coherence length $l_{c}$ [see Eqs. (4) and (5)], (2) an approximately linear increase in intensity with increasing particle size $\hat{r}$ for $\hat{r} \ll \hat{l}_{c}$, and (3) an inverse relation between intensity and particle size (i.e., $I^{2 \omega} \propto 1 / \hat{r}$ ) for $\hat{r} \gg l_{c}$. The approximate range of particle sizes for each experimental point in Fig. 4 is indicated by the horizontal bars.

Similar characteristic features of the particle-size dependence are exhibited by powders immersed in nearly index-matching liquids, as illustrated in Fig. 5 for quartz. The width of particle-size distributions for each experimental point was considerably narrower in the case of quartz (as compared to ZnO ) and evidence of structure for average particle sizes slightly larger than $\hat{l}_{c}$ is seen to appear. Structure of this form is consistent with the theory and is discussed in Sec. IV.

Figure 6 shows a plot of the second-harmonic intensity vs particle size for ADP $\left[\left(\mathrm{NH}_{4}\right) \mathrm{H}_{2} \mathrm{PO}_{4}\right]$ powders in a liquid of nearly matching refractive index (i.e., $n=1.51$ ). For large particle sizes $\left(\hat{r} \gg \hat{l}_{c}\right)$, the second-harmonic intensity is essentially independent of particle size. This is in striking contrast to $\mathrm{SiO}_{2}$ and ZnO (see Figs. 4


Fig. 6. Particle-size dependence of second-harmonic intensity from ADP powders in index-matching liquid,
and 5), where the intensity is inversely proportional to $\hat{r}$ for this range of particle sizes. This difference in behavior is due to the existence of a phase-matching direction ${ }^{13}$ in ADP and is in agreement with the theory presented in the next section. It is in fact the striking difference in particle-size dependence which enables one to distinguish phase-matchable materials on the basis of second-harmonic measurements in powders.

## IV. THEORY

It is obvious at the outset that a number of simplifing assumptions are necessary to reduce a theoretical analysis of SHG in powders to manageable proportions. If the simplifications are sound, the rigor can be regained when more extensive and detailed experimental data are available. In this section we are primarily concerned with deriving expressions which will give a reasonable semiquantitative explanation of the experimental data presented in Sec. III and at the same
time demonstrate how the division into SHG classes is accomplished.

We make the following basic assumptions:
(1) The particles are immersed in a transparent liquid medium of nearly matching refractive index.
(2) The particles are single crystallites of nearly identical size, random orientation, and densely packed (e.g., form factors, polycrystallinity, and voids are neglected).
(3) With appropriate modifications (such as averaging over angles) the theoretical expressions for second-harmonic generation in single-crystal planeparallel slabs can be used in the solution of the problem.

## A. The Single-Particle Equations

Using the results of Kleinman ${ }^{14}$ and Bloembergen, ${ }^{15}$ one arrives at the following expression for the electric field amplitude of the second-harmonic wave in a cubic crystal

$$
\begin{align*}
E_{\perp}{ }^{T}=4 \pi P_{\perp}{ }^{N L S}\left\{-1 /\left(n_{2 \omega} \cos \theta_{T}+\cos \theta_{s}\right)\right. & \left(n_{2 \omega} \cos \theta_{T}+n_{\omega} \cos \theta_{8}\right) \\
& \left.+\exp \left[i(2 \omega / c)\left(n_{\omega} \cos \theta_{s}-n_{2 \omega} \cos \theta_{T}\right) z\right] /\left(n_{\omega}^{2}-n_{2 \omega}{ }^{2}\right)\right\} \exp \left(i \mathbf{k}_{T} \cdot \mathbf{r}-i 2 \omega t\right) \tag{3}
\end{align*}
$$

The notation differs somewhat from that of Bloembergen ${ }^{15}$ in that the symbols have the following definitions:
$\omega=$ frequency of fundamental optical wave,
$P_{L^{N L S}}=$ component of nonlinear optical polarization in direction $\perp$ to plane of transmission,
$n_{\omega}=$ index of refraction of nonlinear medium at angular frequency $\omega$,
$\theta_{s}=$ angle of transmission for polarization wave ( $\mathbf{k}_{s}$ ) measured from $z$ axis,
$\theta_{T}=$ angle of transmission for homogeneous wave $\mathbf{k}_{T}$ measured from $z$ axis,
$z=$ distance along surface normal of medium ( $z=0$ at surface).

Equation (3) is completely general in that $n_{\omega}$ and $n_{2 \omega}$ can be complex [e.g., one can include the effects of optical absorption in Eq. (3)]. For normal incidence ( $\cos \theta_{T}=\cos \theta_{s}=1$ ), one can manipulate Eq. (3) to obtain an expression for the transmitted second-harmonic intensity $I_{\text {ext }}{ }^{2 \omega}$ in terms of the incident intensity $I_{\text {ext }}{ }^{\omega}$ ( $I_{\text {ext }}$ being the intensity external to the slab)

$$
\begin{align*}
I_{\mathrm{ext}}{ }^{2 \omega} c / 8 \pi & =4 n_{2 \omega}{ }^{2} /\left(n_{\omega}+n_{2 \omega}\right)^{2} \\
\times & \times\left[64 \pi l_{c} d^{2 \omega} I_{\mathrm{ext}} \omega / \lambda\left(n_{\omega}+1\right)^{2}\left(n_{2 \omega}+1\right)\right]^{2} \\
& \times\left\{(1-a)^{2}+4 a \sin ^{2}\left[(\pi / 2)\left(r / l_{c}\right)\right]\right\} \tag{4}
\end{align*}
$$

[^5]where the parameters not previously defined are
\[

$$
\begin{aligned}
& l_{c}=\text { coherence length }=\lambda / 4\left(n_{2 \omega}-n_{\omega}\right), \\
& r=\text { thickness of plane-parallel slab, } \\
& d^{2 \omega}=\text { nonlinear optical coefficient }\left[d_{i j 2} j^{2 \omega}\right. \\
& \lambda\text { (see Ref. 25) }], \\
& a=\left[\left(n_{\omega}+1\right) /\left(n_{2 \omega}+1\right) /\left(n_{2 \omega}+1\right)\right] \exp [-(\alpha / 2) r], \\
& \alpha= \text { absorption coefficient at second-harmonic fre- } \\
& \quad \text { quency. }
\end{aligned}
$$
\]

In deriving Eq. (4), absorption at the fundamental was assumed to be zero, and the extinction coefficient $k$ (i.e., $\alpha=4 \pi k / \lambda$ ) at the second harmonic was assumed to be small compared to $n_{2 a}$. Miller ${ }^{16}$ has derived an expression similar to Eq. (4). The primary difference between Miller's result and present form is that " $a$ " contains $\exp [-(\alpha / 2) r]$ instead of $e^{-\alpha r}$ (where $\alpha$ is defined here in the customary fashion $\left.I^{2 \omega}(r)=I_{0}^{2 \omega \sigma \alpha r}\right)$. The expression for " $a$ " given here is the correct form. ${ }^{17}$ The terms $\left[4 n_{2 \omega}{ }^{2} /\left(n_{\omega}+n_{2 \omega}\right)^{2}\right]$ and $\left[\left(n_{\omega}+1\right) / n_{2 \omega+1}\right]$ can usually be set equal to unity since $n_{2 \omega}-n_{\omega} \ll 1$ for most materials.
Equation (4) can be generalized without too much difficulty to nonnormal incidence. The resulting ex-

[^6]Table I. ${ }^{3}$ Comparison of calculated and measured second-harmonic powder response relative to quartz standard.

|  |  | $d_{338} / d_{311}$ | $d_{113} / d_{311}$ | $I^{2 \omega} / I_{\text {quarta }}{ }^{2 \omega}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | Calc. | Meas. |
| ZnO |  |  |  |  |  |
| ( $n_{\omega}=1.95, n_{2 \omega}=2.05$ ) | $d_{333}=43, l_{33}=5.3 \mu$ | (-) | (-) | 4.6 | 6 |
|  | $d_{331}=13, l_{31}=4.81 \mu$ | (+) | $(-)$ | 4.8 |  |
|  | $d_{113}=14, h_{15}=6.31 \mu$ | (-) | (+) | 5.5 |  |
|  |  | (+) | (+) | 5.7 |  |
|  |  |  |  |  |  |
| ( $n_{\omega}=2.34, n_{2 \omega}=2.65$ ) | $d_{333}=186,{ }_{33}=1.71 \mu$ | (-) | $(-)$ | 6.2 | 10 |
|  | $d_{311}=96, l_{31}=1.66 \mu$ $d_{113}=105, l_{15}=1.89 \mu$ | $(-)$ | $\stackrel{(+)}{(-)}$ | 8.9 10.6 |  |
|  |  | (+) | (+) | 13.2 |  |
| ZnS |  |  |  |  |  |
| ( $n=2.34$ ) | $d_{333}=180, l_{33}=5.3 \mu$ | $(-)$ | $(-)$ | 31 | 100 |
|  | $d_{311}=90$ | (-) | (+) | 47 |  |
|  | $d_{113}=(90)$ | $(+)$ | $(-)$ | $\begin{aligned} & 64 \\ & 84 \end{aligned}$ |  |
| GaP |  |  |  |  |  |
| ( $n_{\omega}=3.1, n_{2 \omega}=3.51$ ) | $d_{123}=350, l_{123}=1.29 \mu$ |  |  | 11.9 | 15 |
|  | $d_{123}=525, l_{123}=1.29 \mu$ |  |  | 14.0 |  |
| $\begin{aligned} & \mathrm{ADP} \\ & \quad\left(n_{w}=1.48, n_{2 w}=1.53\right) \end{aligned}$ | $d_{123}=2.8, l_{123} \gg 100 \mu$ |  |  | 14 | 15 |
| $\mathrm{LiNbO}_{3}$ $\left(n_{\omega}=2.233, n_{2 \omega}=2.231\right)$ | $\begin{aligned} & d_{333}=320, l_{33}=5.82 \mu \\ & d_{311}=36, l_{31} \gg 100 \mu \\ & d_{222}=19, l_{22}=5.82 \mu \end{aligned}$ |  |  | 860 | 600 |

${ }^{\text {a }}$ Values for $d_{i j k}{ }^{2 \omega}$ are taken from Ref. 25 and are given in units of $10^{-9} \mathrm{~cm} /$ statvolt.
pressions are very complicated and will not be given here. The two primary differences are an angular dependence of the coherence length $l_{c}$ and an additional angular dependence due to reflection losses.

## B. Summing over Particles. Angular Averages for Materials which are not Phase-Matchable

Let us assume for the moment that the fundamental beam strikes each particle at normal incidence. After traversing each particle the beam proceeds to the next in line. In traveling through the powder the beam encounters approximately $L / \hat{r}$ particles, where $\hat{r}$ is the average particle thickness. In order to proceed further and calculate the resultant second-harmonic intensity


Fig. 7. Schematic representation of different particle-size dependences for phase-matchable and non-phase-matchable materials.
we need to specify whether the second-harmonic fields from different particles are phase-correlated or uncorrelated. For particle sizes much larger than an average coherence length (which we shall define in a moment) we assume that the second-harmonic fields generated by different particles are uncorrelated in which case the total second-harmonic intensity is just the sum of the contributions from each individual particle. Since each individual particle is assumed to have arbitrary orientation and the fundamental traverses a large number of particles we can calculate the contribution per particle by performing a suitable average of $I^{2 \omega}[\mathrm{Eq}$. (4) $]$ over all angles.

The major angular dependent term in Eq. (4) is $d^{2 \omega}$ since this is the component of a third-rank tensor whose principal axis system coincides with the crystallographic axes. For noncubic materials, the coherence length $l_{c}\left[=\lambda / 4\left(n_{2 \omega}-n_{\omega}\right)\right]$ will also depend on angular orientation through $n_{2 \omega}$ and $n_{\omega}$. Since we are excluding phasematchable materials in this section (i.e., materials for which $n_{2 \omega}-n_{\omega} \longrightarrow 0$ for certain directions of propagation) we can define an average coherence length

$$
\begin{equation*}
\hat{l}_{c} \equiv\left\langle\lambda / 4\left(n_{2 \omega}-n_{\omega}\right)\right\rangle_{\mathrm{av}} \tag{5}
\end{equation*}
$$

and proceed to deal separately with the angular averaging of $d_{i j k}{ }^{2 \omega}$. For phase-matchable materials one cannot indulge in this simplification but must include the angular dependence of $l_{c}$ explicitly before taking the angular averages. There is of course an intermediate


Fig. 8. Plot of second-harmonic intensities (relative to quartz standard) as a function of index of refraction, showing division into SHG classes.
area of materials which are "almost" phase-matchable. The present treatment applies where the maximum birefringence is substantially less than the dispersion (e.g., in a negative uniaxial material with birefringence equal to $\frac{1}{4}$ of the dispersion, the maximum variation in coherence length is $\sim 30 \%$ ).
The problem of angular averages for second-order polarizability tensors (such as $d_{i j k^{2 \omega}}{ }^{2 \omega}$ ) has been treated by Cyvin, Rauch, and Decius. ${ }^{18}$ By introducing the direction cosines $\Phi_{F i}$ relating a laboratory-fixed coordinate system $F, G, H$ to a molecule (particle)-fixed system and utilizing the tensor transformation properties

$$
\beta_{F G H}=\sum_{i j k} \Phi_{F i} \Phi_{G j} \Phi_{H k} \beta_{i j k},
$$

the above authors arrive at expressions for $\left\langle\beta_{F G H^{2}}\right\rangle$ of the form

$$
\begin{align*}
& \left\langle\beta_{F F F}{ }^{2}\right\rangle=1 / 7 \sum_{i} \beta_{i i i}{ }^{2}+(6 / 35) \sum_{i \neq j} \beta_{i i i} \beta_{i j j}+(9 / 35) \\
& \quad \times \sum_{i \neq j} \beta_{i i j}+6 / 35 \sum_{i j k \text { cyclio }} \beta_{i j j} \beta_{j k k}+(12 / 35) \beta_{i j k^{2}}^{2} \tag{6}
\end{align*}
$$

and two similar expressions for $\left\langle\beta_{F G G}{ }^{2}\right\rangle$ and $\left\langle\beta_{P G H}{ }^{2}\right\rangle$. Using their results one can obtain expressions for $\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle$ in the laboratory reference frame for the various crystal-symmetry classes exhibiting second generation. Some of these results for $\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle$ are given in the Appendix. Replacing ( $\left.d^{2 \omega}\right)^{2}$ in (4) by its appropriate average and setting $\alpha=0$ we obtain the total secondharmonic intensity from the powder for $\hat{r} \gg l_{c}$

$$
\begin{align*}
I_{\mathrm{tota1}}{ }^{2 \omega} \cong & \frac{32 \pi}{c}\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle\left[\frac{64 \pi I_{\mathrm{ext}}{ }^{\omega}}{\lambda\left(n_{\omega}+1\right)^{2}\left(n_{2 \omega}+1\right)}\right]^{2} \\
& \times L \frac{\hat{l}_{c}^{2}}{\widehat{r}} \sin ^{2}\left(\frac{1}{2} \pi \frac{\hat{r}}{l_{c}}\right) . \tag{7}
\end{align*}
$$

[^7]It is of course very difficult to obtain powders having an exact particle size $r$. In practice there will always be a distribution about some mean value $\hat{r}$. If the rms deviation of $r$ from $\hat{r}$ exceeds $l_{c}$, then the oscillatory behavior due to $\sin ^{2}\left[(\pi / 2)\left(r / \hat{l}_{c}\right)\right]$ will be smeared out and we can replace this term by $\frac{1}{2}$. For particle-size distributions having a $\pm 10 \%$ spread one would expect to see some moderate oscillatory behavior in the region $\hat{l}_{c} \leqq \hat{r} \leqq 3$ to $5 \hat{l}_{c}$. This has indeed been observed in studies of quartz powders (see Fig. 5) where noticeable minima have been observed at $2 \hat{l}_{c}$ and $4 \hat{l}_{c}$. The dominant particle-size dependence however comes from the $L / \hat{r}$ term in Eq. (7) which leads to an inverse relation between mean particle size and second-harmonic intensity. For $\hat{r} \ll l_{c}$, one is tempted to replace $\sin ^{2}\left[(\pi / 2)\left(\hat{r} / \hat{l}_{c}\right)\right]$ in Eq. (7) by $\left[(\pi / 2)\left(\hat{r} / \hat{l}_{c}\right)\right]^{2}$, which leads to $I^{2 \omega} \propto \bar{r} L$ which agrees with the observed behavior (see Fig. 4). When the particle size is much less than the average coherence length the assumption of lack of correlation between harmonic generated in different particles is much more difficult to justify and may in fact be incorrect. An alternative approach which leads to the same result (i.e., $I^{2 \omega} \propto \hat{r} L$ ) assumes that the second-harmonic fields from different particles are correlated provided the particles are separated by a distance which is less than a coherence length. Breaking the cell thickness up into $N$ regions ( $N \equiv L / \hat{l}_{c}$ ), each of which contains $N^{\prime}=\hat{l}_{c} / \hat{r}$ particles, we treat the nonlinear polarization $P^{N L S}$ within each of the $N$ regions by a one-dimensional random-walk model where the step length is proportional to $d^{2 w}$. The net contribution of each region to second-harmonic intensity is then proportional to $\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle / N^{\prime}$ giving a total intensity from all $N$ regions

$$
\begin{equation*}
I_{\mathrm{total}^{2 \omega}}{ }^{2 \omega} N\left[\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle / N^{\prime}\right]=L \hat{r} / \hat{l}_{c}{ }^{2}\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle . \tag{8}
\end{equation*}
$$

We shall not carry our discussion of this case any further, except to point out that in this regime we are

Table II. Summary of powder survey results: SHG class A.

| Material | Pt. group | Part. size | Color | $I^{\omega /} / I_{\text {quartz }}{ }^{2 \omega}$ | SHG class | Refractive index | , Comments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{LiNbO}_{3}$ | $3 m$ | 75-150 $\mu$ | white | 600 | A | $\begin{aligned} & N o=2.286 \\ & N e=2.200 \end{aligned}$ | Known: for comparison only |
| $\mathrm{HIO}_{3}$ | 222 | 75-150 $\mu^{\text {a }}$ | white ${ }^{\text {b }}$ | 300 | A | $N x=2.0103$ | 101 cleavage (J. P. Remeika) |
| $\mathrm{KIO}_{3} \cdot 2 \mathrm{HIO}_{3}$ |  | ungraded | white | 40 | A (or B? ) | $\begin{aligned} & N y=1.9829 \\ & N z=1.8547 \end{aligned}$ |  |
| $\mathrm{KIO}_{3}$ |  | $75-150 \mu$ | white | 1200-2400 | A | $\begin{aligned} & N x=1.700 \\ & N y=1.828 \\ & N z=1.832 \end{aligned}$ |  |
| $\mathrm{LiIO}_{3}$ | 6 | 75-150 $\mu$ | white | 300 | A |  | Difficult to grow (J. G. Bergman) |
| $\mathrm{Ag}_{2} \mathrm{HgI}_{4}$ | $\overline{4} 2 m$ | 5-10 $\mu$ | yellow | 1500 | A |  | (J. G. Bergman) |
| $\mathrm{Cu}_{2} \mathrm{HgI}_{4}$ | $\overline{4} 2 m$ | 5-10 | Org. red | 200 | A |  |  |
| $\mathrm{KNbO}_{3}$ | $m m 2$ | 75-150 $\mu^{\text {a }}$ | white ${ }^{\text {b }}$ | 2000 | A | ( $N \sim 2.4$ ) | Mostly single domain (A. Linz) |
| $\mathrm{PbTiO}_{3}$ | $4 m m$ | 75-150 $\mu^{\text {a }}$ | off-white ${ }^{\text {c }}$ | 2400 | A |  | Gerson (J. Barshataky) |
| $\left[\mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{NO}_{2}\right)_{2}\right]$ | $m m 2$ | $25 \mu$ | light yellow | 500 | A | $\begin{aligned} N x & =1.432 \\ N z & =1.839 \end{aligned}$ | $M$-dinitrobenzene (010) optic plane |
| $\mathrm{ON}\left(\mathrm{CH}_{2}\right)_{2}$ | $\overline{4} 2 m$ | 75-150 $\mu^{\text {a }}$ | white ${ }^{\text {b }}$ | 400 | A | $\begin{aligned} & N=1.484 \\ & N=1.602 \end{aligned}$ | urea <br> (K. Nassau) |

${ }^{\text {a }}$ Single crystal. $\quad{ }^{\mathrm{b}}$ Transparent. ${ }^{\text {c Yellow-green. }}$
dealing with a fluctuation phenomena which vanishes in the limit $N^{\prime} \rightarrow \infty$ (i.e., $\hat{r} \rightarrow 0$ ).

Let us now turn to the more interesting case of materials in which $l_{c}$ becomes very large for some particular crystal orientations (with respect to the incident fundamental beam).

## C. Summing Over Particles. Angular Averages for Phase-Matchable Materials

For certain directions of light propagation in uniaxial and biaxial crystals Maker et al. ${ }^{19}$ and Giordmaine ${ }^{20}$ have shown that phase matching can occur between the polarization wave [e.g., traveling with velocity $\left.c / n_{o}(\omega)\right]$ and the transmitted second-harmonic wave [e.g., traveling with velocity $\left.c / n_{e}(2 \omega)\right]$. For these directions the coherence length becomes very large (and can in certain cases be infinite). The angular width over which phase matching occurs is generally very small and hence only a small fraction of the particles will have the correct orientation.

Thus, the problem of angular averaging is distinctly different from that treated in the previous section. The major fraction of the angular dependence is now in the coherence length rather than the nonlinear coefficient $d^{2 \omega}$. In the vicinity of the phase-matched direction the coherence length can be written ${ }^{21}$

$$
\begin{equation*}
l_{c}=\pi / 2 \beta\left(\theta-\theta_{m}\right), \tag{9}
\end{equation*}
$$

[^8]where
\[

$$
\begin{equation*}
\beta \equiv\left(\omega n_{\omega}{ }^{\circ} / c\right) \sin \rho, \tag{10}
\end{equation*}
$$

\]

$\theta_{m}=$ angle between phase-matching direction and optic axis, $\theta=$ angle between direction of fundamental wave and optic axis, $n_{\omega}{ }^{0}=$ ordinary refractive index at fundamental frequency, $\omega=$ angular frequency of the fundamental, $\rho \equiv$ angle between ellipse and sphere index surfaces at matching.

$$
\tan \rho=\frac{1}{2}\left(n_{\omega}^{o}\right)^{2}\left[1 /\left(n_{2 \omega}^{e}\right)^{2}-1 /\left(n_{2 \omega}{ }^{o}\right)^{2}\right] \sin 2 \theta_{m},
$$

where $n^{e}=$ extraordinary refractive index.
For small birefringence [i.e., $\left(n_{2 \omega}{ }^{e}-n_{2 \omega}{ }^{o}\right) / n_{2 \omega} \ll 1$ ] and small dispersion [i.e., $\left(n_{2 \omega}-n_{\omega}\right) / n_{2 \omega} \ll 1$ ]

$$
\begin{equation*}
\tan \rho \cong \rho \cong\left(n_{2 \omega}{ }^{o}-n_{2 \omega}{ }^{e}\right) / n_{2 \omega} . \tag{11}
\end{equation*}
$$

Substituting Eqs. (10) and (11) into Eq. (9), we obtain

$$
\begin{equation*}
l_{c} \cong \lambda / 4\left(n_{2 \omega}{ }^{e}-n_{2 \omega^{\circ}}\right)\left(\sin 2 \theta_{m}\right)\left(\theta-\theta_{m}\right) . \tag{12}
\end{equation*}
$$

Substituting Eq. (12) into Eq. (4) (with $a=1$ ) and integrating over-all $\theta$, we obtain

$$
\begin{align*}
& I_{\mathrm{ext}^{2 \omega}}=\left\{(32 \pi / c)\left[64 I_{\text {ext }}{ }^{\omega} / \lambda\left(n_{\omega}+1\right)^{2}\left(n_{2 \omega}+1\right)\right]^{2}\right\} \\
& \times\left(d_{\mathrm{PM}}{ }^{2 \omega}\right)^{2}\left[\left(\pi^{2} / 4\right) L \Gamma_{\mathrm{PM}}\right] \tag{13}
\end{align*}
$$

where

$$
\Gamma_{\mathrm{PM}} \equiv \pi \sin \theta_{m} / \beta
$$

and

$$
\hat{r} \gg \Gamma_{\mathrm{PM}} / \sin \theta_{m}
$$

and $d_{\mathrm{PM}}{ }^{2 \omega}$ is that $d_{i j k}{ }^{2 \omega}$ (or combination of $d_{i j k}{ }^{2 \omega}$ 's) for which phase matching occurs.

Table III. Summary of powder survey results: SHG class B.

| Material | Pt. group | Part. size | Color | $R /$ quartz | SHG class | Refractive index | Comments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\left(\mathrm{NH}_{4}\right) \mathrm{H}_{2} \mathrm{PO}_{4}$ | $\overline{4} 2 m$ | 75-150 $\mu$ | white | 15 | B | $\begin{aligned} & N o=1.5215 \\ & N e=1.4768 \end{aligned}$ | Known: for comparison only |
| $\mathrm{LiClO}_{4} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ | 6 mm | 75-150 $\mu^{\text {a }}$ | white ${ }^{\text {b }}$ | 15 | B | $\begin{aligned} & N o=1.483 \\ & N e=1.448 \end{aligned}$ |  |
| $\mathrm{NaNO}_{2}$ | $m m 2$ | ungraded | white | 100 | B | $\begin{aligned} & N x=1.354 \\ & N z=1.648 \end{aligned}$ |  |
| $\mathrm{Ba}\left(\mathrm{CHO}_{2}\right)_{2}$ | 222 | ungraded ${ }^{\text {a }}$ | white ${ }^{\text {b }}$ |  | B | $\begin{aligned} & N x=1.573 \\ & N y=1.597 \\ & N z=1.636 \end{aligned}$ | (001) cleavage (010) optic plane (W. Bond) |
| $\mathrm{C}_{24} \mathrm{H}_{18}$ | $m m 2$ | 10-50 $\mu$ | white |  | B | $\begin{aligned} & N x=1.5242 \\ & N z=1.8725 \end{aligned}$ | (010) optic plane 1,3,5-triphenyl benzene |
| $\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{O}_{6}$ | 2 | 75-150 $\mu^{\text {a }}$ | white ${ }^{\text {b }}$ | 15 | B | $\begin{aligned} & N x=1.4957 \\ & N y=1.6045 \\ & N z=1.5352 \end{aligned}$ | tartaric acid (100) cleavage |
| $\mathrm{C}_{6} \mathrm{H}_{4}(\mathrm{OH})_{2}$ | $m m 2$ | 75-150 $\mu^{\text {a }}$ | white ${ }^{\text {b }}$ | 20 | B | $\begin{aligned} & N x=1.5725 \\ & N z=1.6208 \end{aligned}$ | resorcinol (001) optic plane |
| $\mathrm{Pb}\left(\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right) \cdot 3 \mathrm{H}_{2} \mathrm{O}$ |  | ungraded | white | 35 | B |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{2}\left(\mathrm{NO}_{2}\right)_{3} \mathrm{OH}$ | $m m 2$ | 125-150 $\mu$ | yellow | 60 | B | $\begin{aligned} & N x=1.68 \\ & N z=1.742 \end{aligned}$ | picric acid (explosive) |
| $\mathrm{C}_{16} \mathrm{H}_{16} \mathrm{O}_{2} \mathrm{~N}_{2}$ |  | $25 \mu$ | yellow | 30 | B |  | $P$-anisalazine |
| $l$-histidine | 222 | $25 \mu$ | white | 10 | B? |  |  |
| 4 aminopyridine |  | 25-50 $\mu$ | off-white | 20 | B |  |  |
| $l$-glutamic acid | 222 | 100-150 $\mu$ | white | 8 | B | $\begin{aligned} & N x=1.480 \\ & N z=1.6187 \end{aligned}$ |  |
| $\mathrm{C}_{10} \mathrm{H}_{13} \mathrm{~N}_{5} \mathrm{O}_{4}$ | 2 | ungraded | white |  | B |  | adenosine |
| $\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}$ | 2 | 5-15 $\mu$ | white | 20 | B | $\begin{aligned} & N x=1.517 \\ & N z=1.555 \end{aligned}$ | -lactose |
| $\mathrm{C}_{6} \mathrm{H}_{14} \mathrm{~N}_{2} \mathrm{O}_{2} \cdot \mathrm{HCl}$ | 2 | 25-75 $\mu$ | white |  | B |  | $l$-lysine monohydrochloride |
| $\left(\mathrm{CH}_{3} \mathrm{CHO}\right)_{4}$ | 4 | 75-125 $\mu$ | white | 10 | B |  |  |
| $\mathrm{RbClO}_{3}$ | $3 m$ | $75-150 \mu$ | white | 20 | B | $\begin{aligned} & N x=1.4674 \\ & N y=1.4684 \\ & N z=1.4715 \end{aligned}$ |  |

${ }^{\text {a }}$ Single crystal. b Transparent. ${ }^{\text {e Yellow-green. }}$
Equation (13) is independent of particle size $r$, consistent with the experimental results of Sec. III (see Fig. 6) for large $\widehat{r}$. For $\hat{r} \leqq \Gamma_{\mathrm{PM}} / \sin \theta_{m}$, Eqs. (9)-(13) are no longer valid approximations. While a detailed solution for this region has not been obtained, it can be shown by arguments similar to those used in deriving Eq. (8) that $I_{\text {ext }}{ }^{2 \omega}$ decreases with decreasing $\hat{r}$ in this region. The other nonlinear coefficients $d_{i j k^{2}}{ }^{2 \omega}$ (for which phase matching is not possible) will also contribute to the second-harmonic intensity but in the form derived for non-phase-matchable materials, namely,

$$
\begin{align*}
I_{\mathrm{ext}}{ }^{2 \omega}=\left\{( 3 2 \pi / c ) \left[64 I_{\mathrm{ext}}{ }^{\omega} / \lambda\left(n_{\omega}\right.\right.\right. & \left.\left.+1)^{2}\left(n_{2 \omega}+1\right)\right]^{2}\right\} \\
& \times\left\langle d_{i j k^{2}}{ }^{2}\right\rangle\left[L\left(\hat{l}_{c}\right)^{2} / 2 \hat{r}\right] . \tag{14}
\end{align*}
$$

For sufficiently large particle sizes $\left(\hat{r} \gg \hat{i}_{c}\right)$ this contribution will be small compared to that in Eq. (13) and can be neglected.

When the nonlinear coefficients $d_{i j}{ }^{2 \omega \omega} k$ and coherence lengths $l_{c}$ are known, it is possible to evaluate the ratio of second-harmonic intensities for powders of any two materials using the results given in Eqs. (13) and (14). Assuming identical particle size $\hat{\gamma}\left(\gg l_{c}\right)$ and fundamental intensity $I_{\text {ext }}{ }^{\omega}$, this intensity ratio has been calculated (relative to quartz) for six materials. The results are shown in Table I and are seen to be in reasonable agreement with experiment.

## D. Division into SHG Classes

Based on the foregoing analysis of SHG in powders one can develop a useful division of nonlinear optical materials into five distinct classes. Crude definitions of these five classes were given in Sec. I. In order to be more specific let us write down the expressions for the intensities in both the phase-matched and unphase-

Table IV. Summary of powder survey results: SHG class C.

| Material | Pt. group | Part. size | Color | $R /$ quartz | SHG class | Refractive index | Comments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ZnO | 6 mm | $75-150 \mu$ | white | 15 | C | $\begin{aligned} & N o=2.056 \\ & N e=2.072 \end{aligned}$ | Known: for comparison only |
| $\mathrm{BaTiO}_{3}$ | 4 mm | 75-150 $\mu$ | light green | 130 | C |  | Known: for comparison only |
| CuI | $43 m$ | $25 \mu$ | $\tan$ | 3 | C | $N=2.345$ |  |
| InP | $\overline{4} 3 m$ | 5-15 $\mu$ | black | 4 | C | $N=3.0-3.3$ | (E. Kolb) |
| CdTe | $43 m$ | $10 \mu$ | black | 25 | C | $\begin{aligned} & N x=1.658 \\ & N y=1.662 \\ & N z=1.668 \end{aligned}$ | boracite <br> (K. Nassau) |
| $\mathrm{Sc}_{2}\left(\mathrm{MoO}_{4}\right)_{3}$ |  | $20 \mu$ |  |  | C |  | (K. Nassau) |
| $\mathrm{Gd}_{2}\left(\mathrm{MoO}_{4}\right)_{3}$ |  | 75-150 $\mu$ |  | 20 | C |  | (K. Nassau) |
| $\mathrm{Bi}_{4} \mathrm{Ge}_{3} \mathrm{O}_{12}$ | $43 m$ | 75-150 $\mu^{\text {a }}$ | yellow ${ }^{\text {b }}$ | 6 | C | $n=2.07$ | (A. A. Ballman) |
| $\mathrm{Bit}_{12} \mathrm{GeO}_{20}$ | 23 | $25 \mu$ | yellow | 20 | C |  | (A. A. Ballman) |
| L-SiC | 6 mm | $75-150 \mu$ | white | 8 | C | $\begin{aligned} & N o=2.66 \\ & N e=2.71 \end{aligned}$ |  |
| $\mathrm{N}_{4}\left(\mathrm{CH}_{2}\right)_{6}$ | $43 m$ | 75-150 $\mu$ | white | 8 | C | $N=1.59$ | HMT (K. Nassau) |
| GaP | $\overline{4} 3 m$ | 75-150 $\mu$ | light green | 15 | C | $N=3.31$ |  |
| $\mathrm{Ag}_{3} \mathrm{AsO}_{4}$ | $\overline{4} 3 m$ | 100-150 $\mu$ | dark red | 3 | C |  |  |
| tourmaline | $3 m$ | 75-100 $\mu$ | green | 3 | C | $\begin{aligned} & N o=1.650 \\ & N e=1.628 \end{aligned}$ |  |
| $\mathrm{La}_{2} \mathrm{Ti}_{2} \mathrm{O}_{7}$ |  | 100-150 $\mu$ | pink | 35 | C |  | (L. Mercer) |
| $\mathrm{C}_{6} \mathrm{H}_{14} \mathrm{~N}_{2} \mathrm{O}_{2} \cdot \mathrm{NCl}$ |  | ungraded | white | 4 | C |  |  |
| $\mathrm{BiFeO}_{3}$ | $3 m$ ? | $10 \mu$ | red-brown | 3 | C ( or B?) |  | (R. Gerson) |
| $60 \% \mathrm{BiFeO}_{3}$ |  | $10 \mu$ | red-brown | 40 | C (or B? |  | (R. Gerson) |
| $40 \% \mathrm{PbTiO}_{3}$ |  |  |  |  |  |  |  |
| $\mathrm{LiYbO}_{2}$ | $4 / \mathrm{mm}$ ? | $25 \mu$ | white | 4 | C |  | (G. Peterson) |

${ }^{\mathrm{a}}$ Single crystal. ${ }^{\mathrm{b}}$ Clear yellow.
matched cases. We shall omit all parameters which are identical by virtue of using the same experimental apparatus, powder size, etc.
$I_{\text {ext }}{ }^{2 \omega} \propto\left\langle\left(d_{i j k^{2 \omega}}{ }^{2 \omega}\right)^{2}\right\rangle\left[\left(l_{c}\right)^{2} / 2 \hat{r}\right] \quad$ not phase-matchable

$$
\begin{equation*}
\hat{r} \gg l \tag{15}
\end{equation*}
$$

$$
\begin{align*}
I_{\text {ext }}{ }^{2 \omega} \propto\left(d_{\mathrm{PM}}{ }^{2 \omega}\right)^{2}\left[\left(\pi^{2} / 4\right) \Gamma_{\mathrm{PM}}\right] \quad \text { phase-matchable } \\
\hat{r} \gg \Gamma_{\mathrm{PM}} / \sin \theta_{m} . \tag{16}
\end{align*}
$$

Two additional facts are essential to obtain the desired division into SHG classes. First we note that a particle size $\hat{r}$ of $100 \mu$ generally meets the requirement that $\hat{r}$ be much greater than the average coherence length. In the case of phase-matchable materials it also satisfies the condition $\hat{r} \gg \Gamma_{P M} / \sin \theta_{m}$ [see Eq. (13)] since typical values of $\Gamma_{P M}$ are in the range $1-10 \mu$. It is convenient in this respect to treat the quantity $\Gamma_{\mathrm{PM}} /$ $\sin \theta_{m}$ as a fictitious average coherence length $\hat{l}_{c}$ for the phase-matchable case. Thus, for an average particle size of $100 \mu$ the inequality $\hat{r} \gg l_{c}$ is satisfied for both classes of materials. This region is shown in Fig. 7 to the
right of the vertical dashed line. In this region the phase-matchable materials have attained their maximum second-harmonic intensity independent of particle size, and un-phase-matchable materials, while still varying inversely with particle size, are well away from the region near $l_{c}$ where substantial structure in the second-harmonic intensity occurs (see Fig. 5).
The second fact which is needed for the division into SHG classes is a relation between $d^{2 \omega}$ and refractive index. Miller ${ }^{22}$ has shown from experimental data (and the Garrett ${ }^{23}$-Bloembergen ${ }^{24}$-Robinson ${ }^{25}$ anharmonic oscillator model for SHG have confirmed) that

$$
\begin{equation*}
d^{2 \omega} \propto\left(n_{2 \omega}{ }^{2}-1\right)\left(n_{\omega}{ }^{2}-1\right)^{2} \cong\left(n^{2}-1\right)^{3} . \tag{17}
\end{equation*}
$$

Thus in Eqs. (15) and (16) we can replace $\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle$ and $\left(d_{\mathrm{PM}}{ }^{2 \omega}\right)^{2}$ by $\left(n^{2}-1\right)^{6}$. After making this substitution

[^9]Table V. Summary of powder survey results: SHG class D.

| Material | Pt. group | Part. size | Color | $R /$ quartz | SHG class | Refractive index | Comments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{SiO}_{2}$ | 32 | 75-150 $\mu$ | white | 1 | D | $N o=1.5442$ | Known: for comparison only |
| GaN | 6 mm | 75-125 $\mu$ | green |  | D | $N e=1.5533$ |  |
| $\mathrm{BaTi}\left(\mathrm{SiO}_{3}\right)_{2}$ | $\overline{6} m 2$ | 5-20 $\mu$ | light blue | 1 | D | $\begin{aligned} & N o=1.757 \\ & N e=1.804 \end{aligned}$ | benitoite (K. Nassau) |
| BeO | 6 mm | $10 \mu$ | white | 2 | D | $\begin{aligned} & N o=1.719 \\ & N o \end{aligned}$ |  |
| $\mathrm{CeFCO}_{3}$ | $\overline{6} m 2$ | ungraded | pink | 2 | D | $N o=1.717$ | Bastnasite (K. Nassau) |
| $\mathrm{Ag}_{3} \mathrm{PO}_{4}$ | $\overline{4} 3 m$ | ungraded | yel. ochre | 2 | D |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{13} \mathrm{NO}_{2}$ | 222 | $25 \mu$ | white | 2 | D | $\begin{aligned} & N x=1.5285 \\ & N z=1.5635 \end{aligned}$ | $d$-glucose |
| $\mathrm{CH}_{2} \mathrm{CH}(\mathrm{CHOH})_{3} \mathrm{CHO}$ | 2 | 75-150 $\mu$ | white | 1 | D | $\begin{aligned} & N y=1.549 \\ & N z-N x=0.046 \end{aligned}$ | $d(-)$ ribose |
| $\mathrm{C}_{27} \mathrm{H}_{45} \mathrm{OH}$ | 1 | 25-75 $\mu$ | white | 1 |  | $\begin{aligned} & N y=1.532 \\ & N z-N y=0.046 \end{aligned}$ | cholesterol |
| $\mathrm{Ga}_{4} \mathrm{Fe}_{1-x} \mathrm{O}_{3}$ |  | $<37 \mu$ | reddish-brown | 1/10 | D |  | (J. P. Remeika) |
| $\mathrm{LiErO}_{2}$ | $4 / \mathrm{mmm}$ ? | $25 \mu$ | pink | 1 | D |  | (G. Peterson) |
| $\mathrm{K}_{6} \mathrm{Nb}_{4} \mathrm{O}_{113}$ |  | $10 \mu$ | white |  | D |  | (K. Nassau) |
| $\mathrm{C}_{10} \mathrm{H}_{20} \mathrm{O}$ | 3 | 75-150 $\mu$ | white | 1.5 | D | $\begin{aligned} & N o=1.497 \\ & N e=1.476 \end{aligned}$ | $l$-menthol |

and letting $\hat{r}=100 \mu, l_{c}=10 \mu, \Gamma_{P M}=5 \mu$, we obtain
$I^{2 \omega} \propto 0.5\left[\left(n^{2}-1\right) /(n+1)\right]^{6}\left(l_{c} / 10 \mu\right)^{2} \quad$ NPM
$I^{2 \omega} \propto 12.5\left[\left(n^{2}-1\right) /(n+1)\right]^{6}\left(\Gamma_{\mathrm{PM}} / 5 \mu\right) \quad$ PM.
The division into SHG classes is now evident since we can express (18) and (19) in terms of $I^{2 \omega}$ for quartz ( $n \cong 1.55, \hat{l}_{c} \cong 20 \mu$ ) for different ranges of refractive index $n$

Class D
$I^{2 \omega} / I_{\text {quartz }}{ }^{2 \omega} \leqq 0.43\left(l_{c} / 10 \mu\right)^{2}$ for $n \leqq 1.6 \mathrm{NPM}$
Class C
$I^{2 \omega} / I_{\text {quartz }}{ }^{2 \omega} \geqq 4.6\left(\hat{l}_{c} / 10 \mu\right)^{2} \quad$ for $\quad n \geqq 1.9$ NPM
Class B
$I^{2 \omega} / I_{\text {quartz }}{ }^{2 \omega} \leqq 10.5\left(\Gamma_{\mathrm{PM}} / 5 \mu\right) \quad$ for $\quad n \leqq 1.6 \mathrm{PM}$
Class A
$I^{2 \omega} / I_{\text {quartz }}{ }^{2 \omega} \geqq 115\left(\Gamma_{P M} / 5 \mu\right)$ for $n \geqq 1.9$ PM.
A graphic illustration of these results is shown in Fig. 8. We note that in the assignment of a material to classes B or C, one needs to know whether the refractive index is high or low (i.e., $<1.6$ or $>1.9$ ), which is most easily accomplished for a powder by liquid immersion methods (e.g., the Becke line method). We also note that materials of intermediate refractive index (e.g., $1.6 \leqq n \leqq 1.9$ ) fall in the regions intermediate to A and B or C and D . One could on this basis expand the number of classes from five to seven but there would appear to be little advantage over the scheme chosen here.

## V. MATERIALS SURVEY

## A. Experimental Results

The survey results for about 100 inorganic and organic compounds as well as a number of naturally occurring minerals are shown in Tables II-VI.

The measurements given in Tables II-VI were made for powders in air. While the theory developed in the preceding section applied to the index-matched liquid case, the experimental results for ZnO (see Sec. III and Figs. 4 and 5) and other materials indicate that measurements in air are adequate (i.e., the correct ratio to the quartz standard is retained) for assigning materials to the various SHG classes provided one takes care to collect all the second-harmonic flux.

In the case of transparent materials the assignment to SHG classes is relatively straightforward using the limits set for the various classes in Sec. IV. For absorbing materials no adequate theory has been formulated. The results with absorbing materials having known nonlinear properties (e.g., Se, Te) suggest that only materials in classes A-C will exhibit detectable second harmonic in the powder measurement. Very thin layers ${ }^{7}$ were also found to be more desirable in this case

Table VI. Summary of powder survey results: SHG class E.

| Material | Pt. group | Part. size | Color | $R /$ quartz | SHG class | Refractive index | Comments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{H}_{3} \mathrm{BO}_{3}$ | $\overline{3}$ | ungraded | white | 0 | E |  | boric acid |
| $\mathrm{LaAlO}_{3}$ | $\overline{3} m$ | ungraded | white | 0 | E |  | (S. Geller) |
| $\mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{Cl}$ | $6 / m$ | 75-125 $\mu$ | light yellow | 0 | E | $\begin{aligned} & N o=1.6684 \\ & N e=1.6675 \end{aligned}$ | apatite <br> (K. Nassau) |
| $\mathrm{PbMoO}_{4}$ | 4/m | ungraded | off-white | 0 | E | $\begin{aligned} & N o=2.4053 \\ & N e=2.2826 \end{aligned}$ | wulfenite |
| $\mathrm{Gd}_{2} \mathrm{Ti}_{2} \mathrm{O}_{7}$ |  | ungraded | white | 0 | E |  | (L. Mercer) |
| $\mathrm{Pb}_{5} \mathrm{Cl}\left(\mathrm{VO}_{4}\right)_{3}$ | $6 / m$ | $25 \mu$ | yellow-orange | 0 | E | $\begin{aligned} & N o=2.628 \\ & N e=2.505 \end{aligned}$ | vanadinite (K. Nassau) |
| $\mathrm{ZnWO}_{4}$ | $2 / m$ | ungraded | white | 0 | E |  | (L. G. Van Uitert) |
| $\mathrm{Ba}\left(\mathrm{NO}_{3}\right)_{2}$ | $m 3$ | ungraded | white | 0 | E | $N=1.57$ |  |
| $\mathrm{Pb}_{3} \mathrm{MgNb}_{2} \mathrm{O}_{9}$ |  | ungraded | yellow | 0 | E |  | (L. G. Van Uitert) |
| $\mathrm{Hg}\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2}$ |  | ungraded | light yellow | 0 | E |  | mercuricacetate |
| $\mathrm{BiPO}_{4}$ | 622 | ungraded | white | 0 | E |  |  |
| $\mathrm{Ba}\left(\mathrm{BrO}_{3}\right)_{2}$ | $2 / m$ | 75-125 $\mu$ | white | 0 | E |  |  |
| $\mathrm{Pb}(\mathrm{SCN})_{2}$ |  | ungraded | white | 0 | E |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Cl} \cdot \mathrm{CO}_{2} \mathrm{H}$ | $\overline{1}$ | ungraded | white | 0 | E | $N z-N x=0.280$ | $P$-chlorobenzoic acid |
| $\mathrm{CsPbCl}_{3}$ |  | ungraded | white | 0 | E |  | (H. J. Guggenheim) |
| $\mathrm{MgTiO}_{3}$ | $\overline{3}$ | ungraded | white | 0 | E | $\begin{aligned} & N o=2.31 \\ & N e=1.95 \end{aligned}$ | (J. G. Bergman) |
| $\mathrm{MgCO}_{3}$ | $\overline{3} m$ | 25-125 $\mu$ | white | 0 | E | $\begin{aligned} & N_{o}=1.700 \\ & N_{e}=1.509 \end{aligned}$ | magnesite <br> (K. Nassau) |
| $\mathrm{MnCO}_{3}$ | $\overline{3} m$ | 25-125 $\mu$ | pink | 0 | E | $\begin{gathered} N_{o}=1.817 \\ N e=1.597 \end{gathered}$ | rhodochrosite <br> (K. Nassau) |
| $\mathrm{Pb}_{3}\left(\mathrm{PO}_{4}\right)_{2}$ | $6 / m$ | $25 \mu$ | white | 0 | E | $\begin{aligned} & N o=1.970 \\ & N e=1.926 \end{aligned}$ | (K. Nassau) |
| $9(\mathrm{Mn}, \mathrm{Fe}) \mathrm{O} \cdot 8 \mathrm{SiO}_{2} \cdot \mathrm{MnCl}_{2} \cdot 7 \mathrm{H}_{2} \mathrm{O}$ |  | ungraded | pink | 0 | E | $\begin{aligned} & N_{o}=1.664 \\ & N e=1.629 \end{aligned}$ | friedelite (K. Nassau) |
| ( $\mathrm{F}, \mathrm{Cl}$ ) $\left(\mathrm{PbAsO}_{4}\right)_{3} \mathrm{~Pb}_{2}$ | 6/m | 75-150 $\mu$ | yellow | 0 | E | $\begin{aligned} & N o=2.263 \\ & N e=2.239 \end{aligned}$ | mimetite <br> (K. Nassau) |
| $\mathrm{Al}_{2} \mathrm{SiO}_{5}$ | $\overline{1}$ | $150 \mu$ | white | 0 | E | $\begin{aligned} & N x=1.713 \\ & N y=1.722 \\ & N z=1.729 \end{aligned}$ | kyanite <br> (K. Nássau) |
| PbO | mmm | ungraded | yellow | 0 | E | $\begin{aligned} & N x=2.51 \\ & N y=2.61 \\ & N z=2.71 \end{aligned}$ | masicot |
| PbO | 4/mmm | ungraded | red | 0 | E | $\begin{gathered} N o=2.665 \\ N e=2.535 \end{gathered}$ | litharge |
| $\mathrm{Pb}\left(\mathrm{IO}_{3}\right)_{2}$ | mmm | ungraded | white | 0 | E | $\begin{aligned} & N x=2.15 \\ & N y=2.15 \\ & N z=2.18 \end{aligned}$ |  |
| $\mathrm{WO}_{3}$ | $2 / m$ | ungraded | white | 0 | E |  |  |



Fig. 9. Angular dependence of second-harmonic intensity in single-crystal $\mathrm{Bi}_{4} \mathrm{Ge}_{3} \mathrm{O}_{12}$.
( $\leqq 100 \mu$ ). At present only qualitative information can be obtained from the results on highly absorbing materials. Rather than develop a theoretical model for this case an increase in the wavelength of the fundamental to a region where the material is transparent at both fundamental and harmonic would appear to be the best solution. A system which will operate in the $1.5 \mu(2 \omega)$ to $3 \mu(\omega)$ region is currently being constructed for this purpose.

Materials in SHG classes A and B are potentially useful in nonlinear optical devices. Single crystals of a number of these materials have been grown or obtained from the sources indicated in the comments column of Tables II-VI. The results to date have confirmed the assignments given in Tables II-VI.

## B. Powder Method as a Test for Center of Symmetry

In addition to those materials which were suggested by calculations ${ }^{5}$ based on recent theoretical models ${ }^{4}$ of the nonlinear coefficients, we purposely included in the survey several materials (e.g., $\mathrm{PbO}, \mathrm{MgTiO}_{3}, \mathrm{PbMoO}_{4}$, etc.) which have a center of symmetry and hence belong to class SHG-E (all third-rank tensor elements vanish ${ }^{26}$ identically due to symmetry restrictions). Some of these latter materials were chosen in that they met all the other requirements for a class SHG-A material (see Sec. IV) except symmetry. Thus, any slight accentric distortion should cause a detectable signal at the second harmonic. This check was considered necessary for guarding against spurious effects due to strain, bulk defects, surface phenomena, etc. No case was found in which a material having a wellestablished crystal structure with a center of symmetry also exhibited second-harmonic generation. The experimental powder system is capable of operating over a wide range, the dynamic range being currently used is about eight orders of magnitude in second-harmonic intensity, the lower limit of which is approximately $10^{-2}$ of the SHG signal from the quartz standard. Any substantial increase in the sensitivity at the lower end will eventually lead to the detection of second-harmonic generation due to higher-order effects (e.g., quadrupole interactions ${ }^{27}$ ) even in centrosymmetric compounds.

[^10]The converse situation of crystals belonging to wellestablished acentric point groups is of interest since if the powder technique is capable of detecting second harmonic in any acentric structures, then it can be used as a sensitive and reliable method for establishing the presence or absence of a center of symmetry. The test most commonly used at present for this determination is the Giebe-Scheibe ${ }^{28}$ piezoelectric test. While further work is needed to establish the relative merits of the SHG powder technique several observations are possible. The optical method will work on very fine powders whereas the piezoelectric test does not work in general when the particle size goes below some specific limit which varies from material to material. ${ }^{29}$ Electrical conductivity has no adverse effects on the optical measurement (provided that free-carrier absorption is not significant). The optical method does however depend on the transparency of the sample at the fundamental and second-harmonic wavelengths (e.g., a negative SHG response is inconclusive when the material is strongly absorbing at either of the aforementioned wavelengths) whereas the piezoelectric test is independent of the optical properties of the material.

There are three crystallographic point groups which present problems for the center of symmetry test. These three point groups (432, 422, and 622) do not contain the inversion operator (i.e., materials in these classes lack a center of symmetry). In spite of this acentric character, materials in these classes are not expected to exhibit SHG. In the case of cubic point 432, the piezoelectric moduli also vanish so that the Giebe-Scheibe technique suffers from the same limitation. In the case of the remaining two point groups 422 and 622 , however, the vanishing of the SHG moduli $d_{i j k}{ }^{(2 \omega)}$ is a consequence of Kleinman's permutation rule, ${ }^{30}$ which does not apply to the piezoelectric case. Thus the SHG powder test may be definitive for absence of a center of symmetry (classes A-D) but the converse (class E ) is only definitive for the trigonal, orthorhombic, monoclinic, and triclinic crystal classes. Further work is in progress to develop the optical powder method for use in determining the presence or absence of a center of symmetry in naturally occurring minerals. ${ }^{31}$
Several examples of materials exhibiting pronounced

[^11]second-harmonic generation (classes A-C), in disagreement with the currently assigned point groups, have been found: $\mathrm{KIO}_{3}(2 / m){ }^{32,33} \mathrm{LiYbO}_{2}(4 / \mathrm{mmm})^{34}$ and $\mathrm{BiFeO}_{3}(\overline{3} m) .{ }^{35}$ One material $\left(\mathrm{LiIO}_{3}\right)$ was found, which while assigned ${ }^{36}$ to an accentric point group (622), appeared to violate the Kleinman symmetry conditions ${ }^{30}$ Recent structural studies ${ }^{37,38}$ have shown the correct point group of $\mathrm{LiIO}_{3}$ to be 6 rather than 622, thus resolving the discrepancy. Additional examples will undoubtedly be uncovered by this method in the future.

## VI. SINGLE-CRYSTAL MEASUREMENTS

In order to provide a check on the assignment of materials to the five SHG classes, measurements are currently being made on single crystals with the apparatus shown in Fig. 2 (see Sec. II.C). While much of the work described in this section is preliminary in nature (e.g., the crystal quality in most cases not being adequate for precise measurements) the data which have been obtained are adequate for verifying the assignments of several materials in Tables II-IV. Specifically we have examined single crystals of $\mathrm{Bi}_{4} \mathrm{Ge}_{3} \mathrm{O}_{12}, \mathrm{HIO}_{3}, \mathrm{LiClO}_{4} \cdot 3 \mathrm{H}_{2} \mathrm{O}, \mathrm{KNbO}_{3}, \mathrm{CO}\left(\mathrm{NH}_{2}\right)_{2}$ and $\mathrm{PbTiO}_{3}$, in order of descending crystal quality.

## A. $\mathrm{Bi}_{4} \mathrm{Ge}_{3} \mathrm{O}_{12}$

Flux-grown crystals ${ }^{39}$ of good optical quality were oriented and cut into (110) sections. The (110) faces were polished optically flat and parallel. A plot of the Terhune-Maker-Savage type ${ }^{27}$ obtained by rotating about the [001] axis with the incident light beam in the (001) plane (polarized perpendicular to the axis of rotation) is shown in Fig. 9. By fitting these data to Eq. (4) $\left[\right.$ with $\alpha=0$, and $\left.r / l_{c}=\lambda L / 4\left(n_{2 \omega} \cos \theta_{T}-n_{\omega} \cos \theta_{\varepsilon}\right)\right]$, we find $l_{c}=3.7 \mu$ and $d_{123}\left(\mathrm{Bi}_{4} \mathrm{Ge}_{3} \mathrm{O}_{12}\right)=4 \times d_{111}\left(\mathrm{SiO}_{2}\right)$, which are both consistent (note: $n=2.07$ ) with a class $C$ material (see Fig. 8). The Miller $\delta_{123}$ calculated from the $d_{123}$ quoted above is $0.8 \times 10^{-6} \mathrm{~cm} / \mathrm{statvolts}$ which is low but still compatible with the average value ${ }^{40}$ of $3( \pm 2) \times 10^{-6} \mathrm{~cm} /$ statvolts.

## B. $\mathrm{HIO}_{3}$

Large crystals (several centimeters on a side) of $\alpha$-iodic acid were grown by Remeika from solution. The

[^12]

Fig. 10. Angular dependence of second harmonic near phasematching direction in a (101) cleavage plate of $\mathrm{HIO}_{3}$.
crystals commonly had several moderately well developed facets ( $m\{110\}, q\{011\}, s\{102\}, x\{1 \overline{1} 2\}$ and $r$ (101\}) consistent with past observations ${ }^{41}$ of the habits of this orthorhombic crystal. Several pinacoids and domes of moderate optical quality and size ( $\sim 2 \times 2 \times 2$ cm ) were obtained. The crystals are colorless and transparent. They belong to the rhombic disphenoidal point group 222 and have lattice constants ${ }^{42}$ $a_{0}=5.5379 \AA, b_{0}=5.8878 \AA, c_{0}=7.7333 \AA$. Perfect cleavage is obtained along (101) faces, and imperfect cleavage along (011) faces.
Optically the crystals are negative biaxial with the principal axes of the indicatrix coincident with the crystallographic unit cell axes, $\alpha\left(a_{0}\right)=1.8547$ (acute bisectrix), $\beta\left(c_{0}\right)=1.9829$ (optic normal), $\gamma\left(b_{0}\right)=2.0103$ (obtuse bisectrix), and $2 V=47^{\circ}$ for $5325 \AA$.
Phase-matched second-harmonic generation has been observed for two processes, one of which is shown in Fig. 10. From these measurements we find $d_{123}{ }^{2 \omega}\left(\mathrm{HIO}_{3}\right) \cong$ $1.5 \pm 0.5 d_{311^{2 \omega}}\left(\mathrm{LiNbO}_{3}\right)$ and $\delta_{123^{2 \omega}}=3.3 \pm 1.1 \times 10^{-6} \mathrm{~cm} /$ statvolt. The Miller $\delta$ is thus close to the expected average $\delta$ (see Sec. VI-A).
Since this material is readily grown from solution ${ }^{43}$ and has a large phase-matchable nonlinear coefficient it could be potentially useful for device applications. As a further check on this possibility, several crystals were subjected to high optical power densities at $4880 \AA$ from an argon laser to see if they were susceptible to "optical damage". ${ }^{44}$ No trace of this deleterious effect was observed up to power densities of $2.5 \times 10^{5} \mathrm{~W} / \mathrm{cm}^{2}$ over periods of time up to 10 min . By way of comparison, $\mathrm{LiNbO}_{3}$ damaged within a few seconds under the same conditions.

[^13]Some birefringence is present at the phase-matching angles [i.e., $\rho \neq 0$, see Eq. (11)] but, using the beam crossing scheme of Ashkin et al., ${ }^{45}$ one should in principle be able to get around this limitation.
Iodic acid is optically active, exhibiting a rotation ${ }^{46}$ of $58.7^{\circ} / \mathrm{mm}$ at $5461 \AA$ and $74.5^{\circ} / \mathrm{mm}$ at $4360 \AA$. For propagation directions well away from the optic axes (tens of degrees) these rotations are greatly reduced and should not present any major difficulty for nonlinear applications. Additional work on the nonlinear properties of iodic acid can be found elsewhere. ${ }^{47}$ The single-crystal results clearly establish that the class A assignment of $\mathrm{HIO}_{3}$ is correct.

## C. $\mathrm{KNbO}_{3}$

A crystal cut from a boule of $\mathrm{KNbO}_{3}$ grown by Linz ${ }^{48}$ by pulling from a melt was found to contain some nearly single domain regions. Phase-matched SHG was observed in these regions with a $d^{2 \omega}$ estimated to be $\sim 4 \times d_{311} \mathrm{LiNbO}_{3}$. We note that Wood ${ }^{49}$ has estimated that the birefringence along the " $c$ " axis is around 0.2, which is consistent with a phase-matching angle $\theta_{m} \sim 90^{\circ}$.

## D. $\mathrm{CO}\left(\mathrm{NH}_{2}\right)_{2}$

Very thin prismatic crystals of urea were grown from an alcohol solution by Nassau. ${ }^{50} \mathrm{~A}$ broad phase-matching peak was observed at an external angle of $\sim 20^{\circ}$ consistent with the large natural birefringence and short path length.

## E. $\mathrm{LiClO}_{4} \cdot 3 \mathrm{H}_{2} \mathrm{O}$

Prismatic crystals of this material have been grown by Storey ${ }^{51}$ from water solution. Measurements were made on a section $\sim 10 \mathrm{~mm} \times 5 \mathrm{~mm} \times 5 \mathrm{~mm}$ of moderate optical quality. Phase matching was observed for $\theta_{m}=22.5^{\circ}$. The nonlinear coefficient $d_{311}$ has been estimated to be slightly smaller than $d_{111}$ of crystalline quartz. The single-crystal measurements are thus consistent with the class C assignment of this material.

## F. $\mathrm{PbTiO}_{3}$

Multidomain crystals of $\mathrm{PbTiO}_{3}$ were grown by Barshatky ${ }^{52}$ from the flux. Phase matching seems to occur near $\theta_{m} \cong 90^{\circ}$ but difficulty was encountered with

[^14]the multidomain character of the crystals and absorption at $2 \omega$ (of unknown origin), making the results somewhat uncertain. It should be noted that the birefringence data of Shirane et al..$^{53}$ ( $\Delta n \cong 0.01$ ) at room temperature are certainly inconsistent with the possibility of phase matching, making further study of the SHG properties essential before any conclusions concerning SHG class can be made.

## VII. CONCLUSIONS

The study of second-harmonic generation in powders has been shown to yield useful information on the nonlinear optical properties of solids. An analysis has shown that the SHG powder data can be used to assign materials to one of five possible classes. Two of these classes contain the phase-matchable materials. The ability of the technique to sort out new phase-matchable materials having large nonlinear coefficients makes it attractive for materials survey work particularly since the difficult requirement of obtaining single crystals of optical quality has been removed. The technique also promises to be a useful adjunct to the piezoelectric test for a center of symmetry.

Using this powder technique in conjunction with recently developed theories which enable one to predict the magnitude of the nonlinear coefficients, one has a powerful combination of tools which should provide a substantial increase in the number of new materials for use in nonlinear optics applications.

The results of an initial survey of approximately 100 compounds are reported. Second-harmonic generation was detected for the first time in 56 of these materials. Twenty-seven have been assigned to the phase-matchable categories. Single-crystal measurements on four of these latter compounds have verified the existence of phase-matching directions for second-harmonic generation. One of these materials $\left(\mathrm{HIO}_{3}\right)$ shows considerable promise for nonlinear optical device applications since in addition to being phase-matchable: (1) It is readily grown from solution. (2) The nonlinear coefficient is about 1.5 times larger than $d_{31}$ in $\mathrm{LiNbO}_{3}$. (3) It does not exhibit optical damage effects.

## ACKNOWLEDGMENTS

The authors wish to thank R. C. Miller and R. A. Laudise for suggesting this work and their continuing interest and encouragement throughout its various phases.

We are especially indebted to the many people who supplied us with the materials which made this study possible, particularly J. G. Bergman, J. P. Remeika, K. Nassau, R. Storey, J. Barshatky, E. Kolb, A. A. Ballman, H. J. Guggenheim, L. G. Van Uitert, and A. Linz.

[^15]A critical reading of the manuscript by J. A. Giordmaine and many helpful suggestions are gratefully acknowledged. Thanks are also extended to D. Kleinman and I. Freund for valuable discussions.
The authors also wish to thank S. Bortas, C. R. Statton, and D. J. Nitti for their skilled assistance in various phases of this work.

## APPENDIX: CALCULATION OF $\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle$ FOR DIFFERENT CRYSTAL POINT GROUPS

For unpolarized fundamental and second harmonic,

$$
\begin{aligned}
\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle= & \left\langle\left(d_{F F P^{2 \omega}}\right)^{2}\right\rangle+\left\langle\left(d_{F G G^{2 \omega}}\right)^{2}\right\rangle+\left\langle\left(d_{F G H^{2 \omega}}\right)^{2}\right\rangle \\
= & (19 / 105) \sum_{i}\left(d_{i i i} i^{2 \omega}\right)^{2}+(13 / 105) \sum_{i \neq j} d_{i i i}{ }^{2 \omega} d_{i j j^{2 \omega}} \\
& +(44 / 105) \sum_{i \neq j}\left(d_{i i j} 2 \omega\right)^{2}+(13 / 105) \\
& \times \sum_{i j k, c y c \mathrm{lic}} d_{i i j}{ }^{2 \omega} d_{j k k}{ }^{2 \omega}+(5 / 7)\left(d_{i j k^{2 \omega}}\right)^{2} .
\end{aligned}
$$

(a) Point group 32 (quartz) has nonzero tensor elements

$$
d_{111^{2 \omega}}=-d_{122^{2 \omega}}=-d_{221}^{2 \omega}
$$

giving

$$
\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle=(50 / 105)\left(d_{111}{ }^{2 \omega}\right)^{2} .
$$

(b) Point groups $\overline{4} 3 m$ and $\overline{4} 2 m$ have nonzero tensor elements

$$
\begin{aligned}
d_{123}{ }^{2 \omega} & =d_{213}{ }^{2 \omega}=d_{312^{2 \omega}} \\
\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle & =(5 / 7)\left(d_{123^{2 \omega}}\right)^{2} .
\end{aligned}
$$

(c) Point groups 6 mm and 4 mm have nonzero tensor elements, $d_{333}{ }^{2 \omega}$

$$
\begin{aligned}
d_{311}{ }^{2 \omega} & =d_{322}{ }^{2 \omega}=d_{222^{2 \omega}}=d_{113^{2 \omega}} \\
\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle= & =(19 / 105)\left(d_{333^{2 \omega}}\right)^{2}+(26 / 105) d_{333^{2 \omega}} d_{311}{ }^{2 \omega} \\
& +(114 / 105)\left(d_{113^{2 \omega}}\right)^{2} .
\end{aligned}
$$

(d) Point group $3 m$ has nonzero tensor elements, $d_{333^{2 \omega}}$

$$
\begin{aligned}
d_{31 \mathbf{1}^{2 \omega}}= & d_{322^{2 \omega}}=d_{223^{2 \omega}}=d_{113^{2 \omega}} \\
d_{211^{2 \omega}}= & d_{112} 2^{2 \omega}=-d_{222}{ }^{2 \omega} \\
\left\langle\left(d^{2 \omega}\right)^{2}\right\rangle= & (19 / 105)\left(d_{333^{2 \omega}}\right)^{2}+(26 / 105) d_{332^{2 \omega}} d_{311^{2 \omega}} \\
& +(114 / 105)\left(d_{113^{2 \omega}}\right)^{2}+(10 / 21)\left(d_{222} 2^{2 \omega}\right)^{2} .
\end{aligned}
$$

# The Nature of Thermally Induced Stresses in Silicon and Their Relation to Observed X-Ray Diffraction and Birefringence Phenomena 

Gene J. Carron and L. K. Walford<br>Research Division, McDonnell Company, St. Louis, Missouri

(Received 21 February 1968)


#### Abstract

The purpose of this paper is to describe qualitatively the residual stress field induced in single-crystal silicon by electron-beam melting and subsequent resolidification in microspot areas. The stress distribution is derived by vector relationship from previously reported experimental observations by x-ray topography and polarized ir radiation techniques. The stresses are distributed in a sixfold pseudohyperbolic form around the microspots. This distribution correlates with the four-lobed x-ray rosettes recorded from various x-ray reflections. The stresses are concentrated normal to the $\{111\}$ planes of the parent lattice and, in projection, all stresses in the $\langle 110\rangle$ directions are tangential to the microspot. Infrared birefringence results from stresses along the $\langle 111\rangle$ directions either within the microspot or at its interface with the parent lattice. These directions thus become uniaxial optic axes coincident with the stress direction. Recrystallization mechanisms are discussed in relation to the macro stacking fault observed by x-ray topography.


## I. INTRODUCTION

The observation by x-ray diffraction topography and polarized ir radiation studies of thermally induced stresses in single-crystal silicon have previously been published. ${ }^{1-3}$ These experiments were confined to the study of microspot solidification and the resulting stresses in thin silicon wafers subsequent to localized electron-beam bombardment. It was reported that four-lobed x-ray rosette patterns and ir birefringence

[^16]could be observed in microspot areas where the stresses had not been relieved by the occurrence of $\{111\}$ cleavage. It is the purpose of this paper to present a qualitative description of the residual stress field induced by microspot solidification and to discuss the birefringence and recrystallization in such areas. In so doing, several unanswered questions which arose from the experimental work can be clarified. This will be helpful in the development of a complete theoretical explanation relating $x$-ray, ir, and optical electromagnetic phenomena.
In particular, the points to which we intend to address ourselves are:
(1) The residual stress distribution surrounding the


[^0]:    ${ }^{1}$ G. D. Boyd, R, C. Miller, K. Nassau, W. L. Bond, and A. Savage, Appl. Phys. Letters 5, 234 (1964).
    ${ }^{2}$ S. A. Akhmanov, A. I. Kovrigin, V. A. Kolosov, A. S. Piskarskas, V. V. Fadeev, and R. V. Khokhlov, JETP Letters 3, 241 (1966); R. C. Miller and W. A. Nordland, Appl. Phys. Letters 10, 53 (1967) ; L. B. Kreuzer, Appl. Phys. Letters 10, 336 (1967); J. E. Geusic, H. J. Levinstein, J. J. Rubin, S. Singh, and L. G. Van Uitert, Appl. Phys. Letters 11, 269 (1967).
    ${ }_{3}$ W. W. Rigrod and I. P. Kaminow, Proc. JEEE 51, 137 (1963); C. J. Peters, Proc. IEEE 51, 147 (1963); R. T. Denton, F. S. Chen, and A. A. Ballman, J. Appl. Phys. 38, 1611 (1967); F. S. Chen, J. E. Geusic, S. K. Kurtz, J. G. Skinner, and S. H. Wemple, J. Appl. Phys. 37, 388 (1966).
    ${ }^{4}$ R. C. Miller, Appl. Phys. Letters 5, 17 (1964) ; C. G. B. Garrett and F. N. H. Robinson, J. Quantum Electron. QE-2, 328 (1966); S. K. Kurtz and F. N. H. Robinson, Appl. Phys. Letters 10, 62 (1967) ; F. N. H. Robinson, Bell System Tech. J. 46, 913 (1967).
    ${ }^{5}$ S. K. Kurtz, Intern. Quantum Electron. Conf. Miami (May 1968) paper 6F-5, IEEE J. Quantum Electron. (to be published).
    ${ }^{6}$ K. F. Hulme, O. Jones, P. H. Davies, and M. V. Hobden, Appl. Phys. Letters 10, 133 (1967); E. H. Turner, IEEE J. Quantum Electron. QE-3, 695 (1967).
    ${ }^{7}$ P. M. Rentzepis and Yo-Han Pao, Appl. Phys. Letters 4, 156 (1964) ; W. L. Peticolas, J. P. Goldsborough, and K. E. Rieckhoff, Phys. Rev. Letters 10, 43 (1963).

[^1]:    ${ }^{8}$ J. Ducuing and N. Bloembergen, Phys. Rev. 133, 1493 (1964); see also Ref. 15, Chap. V, p. 131.

[^2]:    ${ }^{9}$ R. G. Smith and M. F. Galvin, J. Quantum Electron. QE-3, 406 (1967).

[^3]:    ${ }^{10} \mathrm{M}$. Born and E. Wolf, Principles of Optics (The MacMillan Company, New York, 1964), Chap. IV, p. 182.
    ${ }^{11}$ R. Uĺbricht, Das Kugelphotometer ( R . Oldenburg, Munich and Berlin, 1920) ; D. G. Goebel, Appl. Opt. 6, 125 (1967).

[^4]:    ${ }^{12}$ C. K. N. Patel, Phys. Rev. Letters 16, 613 (1966).

[^5]:    ${ }^{13}$ R. W. Terhune, P. D. Maker, and C. M. Savage, Appl. Phys. Letters 2, 54 (1963).

[^6]:    ${ }^{14}$ D. A. Kleinman, Phys. Rev. 128, 1761 (1962).
    ${ }^{15}$ N. Bloembergen, Nonlinear Optics (W. A. Benjamin, Inc., New York, 1965), Chap. 4.
    ${ }^{16}$ R. C. Miller, Proceedings of the International Conference on Ferroelectrics (Inst. of Physics Czech. Acad. Sci., Prague, 1966), Vol. I, p. 407. A slightly different form is given in R. C. Miller and A. Savage, Appl. Phys. Letters 4, 169 (1966).
    ${ }^{17}$ R. C. Miller (private communication).

[^7]:    ${ }^{18}$ S. J. Cyvin, J. E. Rauch, and J. C. Decius, J. Chem. Phys. 43, 4083 (1965).

[^8]:    ${ }^{19}$ P. D. Maker, R. W. Terhune, M. Nisenoff, and C. M. Savage, Phys. Rev. Letters 8, 21 (1962).
    ${ }^{20}$ J. A. Giordmaine, Phys. Rev. Letters 8, 19 (1962).
    ${ }^{21}$ A. Ashkin, G. D. Boyd, and J. M. Dziedic, Phys. Rev. Letters 11, 14 (1963).

[^9]:    ${ }^{22}$ R. C. Miller, Appl. Phys. Letters 5, 17 (1964).
    ${ }^{23}$ C. G. B. Garrett, IEEE J. Quantum Electron. QE-4, 70 (1968).
    ${ }^{24}$ Ref. 15, Chap. I.
    ${ }^{25}$ F. N. H. Robinson, Bell System Tech. J. 46, 913 (1967).

[^10]:    ${ }^{26}$ J. F. Nye, Physical Properties of Crystals, (Oxford University Press, London, 1964).
    ${ }^{27}$ R. W. Terhune, P. Maker, and C. M. Savage, Phys. Rev. Letters 8, 21 (1962).

[^11]:    ${ }^{28}$ E. Giebe and A. Scheibe, Z. Physik 33, 760 (1925).
    ${ }^{29}$ J. P. Remeika (private communication).
    ${ }^{30} \mathrm{D} . \mathrm{A}$. Kleinman, Phys. Rev. 126, 1977 (1962).
    ${ }^{31}$ S. K. Kurtz and K. N. Nassau (unpublished).

[^12]:    ${ }^{32}$ R. W. G. Wyckoff, Crystal Structures (Interscience Publishers, Inc., New York, 1960), 2nd ed., Vol. II, pp. 382, 392, 452.
    ${ }^{33}$ Naray-Szabo, Structure Rept. (Oosthoek, Utrecht, 1947), Vol. 11, p. 455.
    ${ }^{34}$ F. Bertaut and M. Gondrand, Compt. Rend. 255, 1135 (1962).
    ${ }_{35}$ A. I. Zaslavskii and A. G. Tutor, Dokl. Akad. Nauk SSSR 135, 815 (1960); V. S. Filip'ev et al., Kristallografiya 5, 913 (1960).
    ${ }^{36}$ W. H. Zachariasen and F. A. Barta, Phys. Rev. 37, 1626 (1931).
    ${ }_{37}$ J. L. DeBoer, F. Van Bolhuis, Roeli Olthof-Hazekomp, and Aafje Vos, Acta Cryst. 21, 841 (1966).
    ${ }^{38}$ A. Rosenzweig and B. Morosin, Acta Cryst. 20, 758 (1966).
    ${ }^{39}$ R. Nitsche, J. Appl. Phys. 36, 2358 (1965).
    ${ }^{40}$ Calculated from an up-to-date table of values given in Ref. 25, p. 945.

[^13]:    ${ }^{41}$ P. Groth, Chemische Krystallographia (Leipzig, 1906) Vol. I, p. 125 .
    ${ }^{42}$ R. W. G. Wyckoff, Crystal Structures (Interscience Publishers, Inc., New York, 1964), 2nd ed., Vol. II, p. 387.
    ${ }^{43}$ J. J. Gilman, The Art and Science of Growing Crystals (John Wiley \& Sons, New York, 1963), Chap. 11, p. 194.
    ${ }_{44}$ A. Ashkin, G. D. Boyd, J. M. Diedzic, R. G. Smith, A. A. Ballman, H. J. Levinstein, and K. Nassau, Appl. Phys. Letters 9 , 72 (1966).

[^14]:    ${ }^{45}$ A. Ashkin, G. D. Boyd and D. A. Kleinman, Appl. Phys. Letters 6, 179 (1965).
    ${ }^{46}$ International Critical Tables, (McGraw-Hill Book Co., New York, 1929), Vol. VII, p. 353.
    ${ }^{47}$ S. K. Kurtz, J. G. Bergman, Jr., and T. T. Perry, Appl. Phys. Letters 12, 186 (1968) ; S. K. Kurtz, J. G. Bergman, Jr., and T. T. Perry, Bull. Am. Phys. Soc. 13, 388 (1968).
    ${ }^{48}$ Grown by a modified Kyropoulos technique similar to that used for $\mathrm{BaTiO}_{3} ; \mathrm{A}$. Linz, V. Belruss, and C. S. Naiman, Proc. Electrochem. Soc. 112, 60C (1965).
    ${ }^{49}$ E. A. Wood, Acta Cryst. 4, 353 (1951).
    ${ }^{50}$ Grown by evaporation in air at room temperature from saturated solution of urea in methanol.
    ${ }^{51}$ Solution growth on a rotating seed in a Holden crystallizer (A. Holden, The Faraday Symp. on Crystal Growth, Bristol, 1949, Discussion No. 5).
    ${ }^{62}$ Grown from PbO flux at $1100^{\circ} \mathrm{C}$ and cooled at $10^{\circ} \mathrm{C} / \mathrm{h}$.

[^15]:    ${ }^{53}$ G. Shirane, R. Pepinsky, and B. C. Frazer, Acta Cryst. 9, 131 (1956).

[^16]:    ${ }^{1}$ G. J. Carron and L. K. Walford, Appl. Phys. Letters 7, 304 (1965).
    ${ }^{2}$ G. J. Carron, Appl. Phys. Letters 9, 355 (1966).
    ${ }^{3}$ G. J. Carron and L. K. Walford, J. Appl. Phys. 38, 3949 (1967).

