

AD 724300

NRL Report 7273

# An Evaluation of Nonlinear Optical Materials by the Second-Harmonic Powder Technique

J. F. GIULIANI AND L. S. GOLDBERG

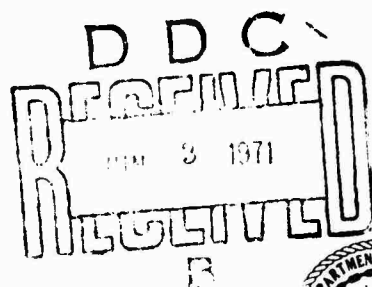
*Quantum Optics Branch  
Optical Sciences Division*

and

F. VON BATCHELDER

*Central Materials Research Activity*

April 29, 1971



Reproduced by  
**NATIONAL TECHNICAL  
INFORMATION SERVICE**  
Springfield, Va 22151

**NAVAL RESEARCH LABORATORY**  
**Washington, D.C.**

### ABSTRACT

The nonlinear optical properties of 21 crystalline materials, principally of the iodate family of compounds, were evaluated using the second-harmonic powder technique developed by Kurtz and Perry. By this method the second-harmonic radiation generated in a powdered sample by a laser at  $1.06 \mu\text{m}$  was compared with a known reference,  $\text{LiIO}_3$  in this case. Of the materials tested, 12 have previously been reported on in the literature, and our results are in substantial agreement.  $\text{KIO}_3$  and  $\text{RbIO}_3$  are identified as having the most promise for crystal development effort. The remaining materials, observed for the first time, failed to exhibit appreciable second-harmonic intensity.

### PROBLEM STATUS

This is a final report on one phase of the NRL Problem.

### AUTHORIZATION

NRL Problem N01-22.501  
Project ARPA Order 306, Amendment 15

Manuscript submitted March 10, 1971.

ACCESSION for	
CFSTI	WHITE SECTION <input checked="" type="checkbox"/>
DDC	BUFF SECTION <input type="checkbox"/>
DATA: ROUNDED	<input checked="" type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
DEST.	AVAIL. and/or SPECIAL
A	

**BLANK PAGE**

# AN EVALUATION OF NONLINEAR OPTICAL MATERIALS BY THE SECOND-HARMONIC POWDER TECHNIQUE

## INTRODUCTION

An important area of research in nonlinear optics is the development of new crystalline materials having suitable nonlinear optical properties. In nonlinear device applications, such as frequency conversion and generation, modulation, and control of optical beams, improvements in performance and in spectral range depend on improved properties of the nonlinear crystals employed.

There are several criteria to consider in determining a crystal's usefulness for nonlinear optical experiments: (a) acentric symmetry class, for nonvanishing second-order nonlinear susceptibility; (b) high transparency in the spectral region of interest; (c) sufficient birefringence to allow phase matching; (d) large nonlinear susceptibility coefficients; (e) good physical characteristics, such as surface hardness and insolubility; and (f) resistance to optical radiation damage.

A recent experimental technique developed by Kurtz and Perry [1,2], and independently studied by Graja [3], allows a rapid initial evaluation of the nonlinear optical properties of crystalline material in powdered form. The technique involves the measurement of laser-induced second-harmonic radiation produced from powdered samples of graded particle sizes. The measured harmonic intensity is then compared quantitatively against a reference material whose nonlinear optical properties are known. By this means a rapid determination can be made whether a material is acentric and whether it has relatively large nonlinear coefficients and is phase matchable. Hence materials that show little promise can be eliminated without requiring the time-consuming growth of single crystals of sufficient size and quality for evaluation.

At NRI, a cooperative research program has been undertaken by the Central Materials Research Activity and the Quantum Optics Branch into the development and growth of nonlinear crystals for use in the visible and infrared spectral regions. This report describes the use of the second-harmonic powder technique at  $1.06 \mu\text{m}$  to investigate several crystals, principally of the iodate family, for their potential as nonlinear materials.

## THEORY

A detailed discussion of the theory of second-harmonic generation in crystalline powders is given in the original paper of Kurtz and Perry [1]. In this section we will sketch their analysis and indicate the basis for distinguishing between phase-matchable (PM) and non-phase-matchable (NPM) materials.

It is assumed that a powdered sample contains graded particles of average thickness  $\hat{r}$ , densely packed in a thin layer of thickness  $L$ , and that the diameter of the laser beam is  $D \gg \hat{r}$  so that a statistically large number of particles of random orientation are encountered. The analysis involves an angular average of the second-harmonic intensity  $I^{2\omega}$  over terms involving the nonlinear tensor susceptibility  $d_{ijk}^{2\omega}$  and the coherence length  $\ell_c = \lambda/4(n_{2\omega} - n_{\omega})$ . For NPM materials an average value for coherence length may be taken, typically of the order 1 to  $10 \mu\text{m}$  at visible wavelengths, and the angular average performed only over  $d_{ijk}^{2\omega}$ ; however, for PM materials, in which  $n_{2\omega} - n_{\omega} \neq 0$  in certain crystal directions, the angular average must include the angular dependence of  $\ell_c$ . A comparison

between the second-harmonic intensity  $I^{2\omega}$  generated from NPM and PM materials and its dependence on average particle size  $\hat{r}$  can be made as follows:

**NPM case.** For  $\hat{r} < \ell_c$ ,  $I^{2\omega}$  increases with particle size, reaching a maximum value at  $\hat{r} = \ell_c$ .  $I^{2\omega}$  then decreases inversely with  $\hat{r}$ , since the second harmonic generated in each particle remains constant while the density of particles in the fixed volume decreases. Thus, for a NPM material in the limit of large  $\hat{r}$  ( $\gg \ell_c$ ),

$$I^{2\omega} \propto (d_{ijk}^{2\omega})_{av}^2 [(\ell_c)^2/2\hat{r}]. \quad (1)$$

**PM case.**  $I^{2\omega}$  increases steadily with particle size and reaches a maximum intensity in the limit  $\hat{r} \gg \ell_c'$ , so long as there are still a statistically large number of particles to be sampled.  $\ell_c'$  is identified here as a fictitious coherence length, related to double refraction in the medium, and is about 1 to 10  $\mu\text{m}$ . Likewise, for a PM material in the limit of large  $\hat{r}$  ( $\gg \ell_c'$ ),

$$I^{2\omega} \propto (d_{PM}^{2\omega})_{av}^2 [(\pi^2/4)\ell_c' \sin \theta_{PM}]. \quad (2)$$

Here  $(d_{PM}^{2\omega})_{av}$  is an average taken only over phase-matchable components and  $\theta_{PM}$  is the phase-matching angle measured from the crystal's optic axis. The constant of proportionality in Eqs. (1) and (2) is identical and involves primarily the refractive indices of the powder at the fundamental and second-harmonic frequencies.

Thus Eqs. (1) and (2) predict a significant difference in the second harmonic intensity for powdered materials according to the magnitude of their nonlinearity and their phase matchability, when measured under identical experimental conditions.

Since the primary purpose of this work was to quickly evaluate a number of untested materials, the second-harmonic intensity was measured for all the materials at a fixed particle size, ensuring, however, that  $\hat{r} \gg \ell_c, \ell_c'$ . A powdered sample of  $\text{LiIO}_3$ , which is phase matchable and has large nonlinearity, was chosen as a reference against which the other materials were compared.

## EXPERIMENTAL

The experimental arrangement is shown in the schematic of Fig. 1. The laser source was Nd:YAG operating at a wavelength of 1.06  $\mu\text{m}$ . It was continuously pumped and repetitively Q-switched at 2 kHz, with an average output power of about 0.1 watt in an unpolarized 3-mm-diameter beam. Powdered samples were prepared by grinding small crystalline pieces and sorting with sieves to obtain particle sizes in the range 74 to 125  $\mu\text{m}$ . The powder was placed in a 2-mm-thick cell with fused quartz windows and irradiated at normal incidence. Second-harmonic light at 0.53  $\mu\text{m}$  was detected by an S-11 photomultiplier placed directly behind the cell. Appropriate glass and interference filters were used to isolate the harmonic radiation. The photomultiplier output was amplified and rectified in a phase-sensitive amplifier, and the resultant dc-level signal was displayed on a strip-chart recorder. A portion of the laser beam was monitored by a photodiode to provide a synchronizing signal for the phase-sensitive amplifier.

The observed second-harmonic signal from a sample of unknown nonlinear properties was then compared with a reference sample of  $\text{LiIO}_3$  powder of size 74 to 125  $\mu\text{m}$  contained in an identical cell. The ratio of these two signals constitutes the comparison of the unknown sample relative to  $\text{LiIO}_3$ . Detection sensitivity was improved by gently focusing the laser beam to a 1-mm diameter at the sample while still allowing a statistically large number of particles to be sampled. The sensitivity was adequate to measure signals three

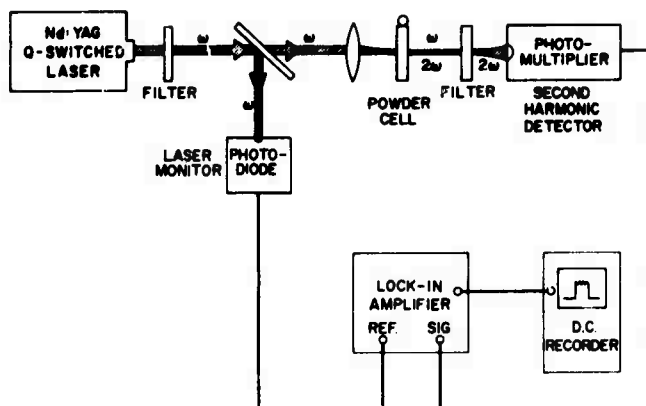


Fig. 1 - Arrangement of the experiment

orders of magnitude weaker than those produced in the  $\text{LiIO}_3$  reference sample. No attempt was made to use index-matching liquids or an integrating sphere to minimize the effects of scattering from the powdered samples.

## DISCUSSION OF RESULTS

The results of our powder measurements are presented in Table 1 for 21 crystalline materials. The ratio of second-harmonic intensity observed for each material relative to a powdered  $\text{LiIO}_3$  standard is tabulated in the fourth column. The ratios of previously measured materials, which have been renormalized to  $\text{LiIO}_3$  for ease of comparison, are shown in the fifth column. The sixth column indicates the method of preparation of the materials studied in this report.

Sixteen of the materials investigated were iodate compounds. Eight of these had not previously been measured either as single crystals or by the powder technique. They were  $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}(\text{IO}_3)_2$ ,  $\text{Co}(\text{IO}_3)_2$ ,  $\text{Cu}(\text{IO}_3)_2$ ,  $\text{Cu}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Zn}(\text{IO}_3)_2$ ,  $\text{AgIO}_3$ , and  $\text{Cd}(\text{IO}_3)_2$  and are indicated by dashes in the fifth column. None of these new iodate compounds showed appreciable second-harmonic intensity, indicating low nonlinear coefficients or lack of sufficient birefringence for phase matching.  $\text{Co}(\text{IO}_3)_2$ ,  $\text{Cu}(\text{IO}_3)_2$ , and  $\text{Cu}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$  show absorption structure in the visible, and this may contribute in part to a reduction in their observed second-harmonic intensity.

Two of the previously measured group of iodates,  $\text{KIO}_3$  and  $\text{RbIO}_3$ , exhibited second-harmonic intensities greater than for  $\text{LiIO}_3$ . Literature values [1,2,4,5] for  $\text{KIO}_3$  are in wide disagreement and indicate a harmonic intensity as much as a factor of 2 greater than for  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ , one of the leading nonlinear materials. Our measurements show  $\text{KIO}_3$  to have a harmonic intensity slightly lower than for  $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ . Similarly  $\text{RbIO}_3$  is found to have a harmonic intensity not nearly as large as previously reported [4] although somewhat larger than for  $\text{LiIO}_3$ . Hence, both  $\text{KIO}_3$  and  $\text{RbIO}_3$  show promise as potential nonlinear materials, and efforts at single-crystal growth should be pursued.

Three organic dye crystals previously investigated by Bass et al. [5] were measured. The best of these,  $\text{C}_{14}\text{H}_{17}\text{NO}_2$ , showed less second-harmonic intensity than did  $\text{HIO}_3$ .

## SUMMARY

The second-harmonic powder technique has provided with modest experimental effort a rapid means of evaluating the nonlinear optical properties of crystalline materials at

Table 1  
Summary of Second-Harmonic Powder Measurements

Material	Point Group	Color	Measured Ratio	Literature Ratio	Material Preparation
$\text{LiIO}_3$	6	White	1.00	1.00	Grown from aqueous solution; slow evaporation, at room temperature or from hot solutions.
$\text{HIO}_3$	222	White	0.75	1.00*, 1.27†	Same as above.
$\text{NH}_4\text{IO}_3$	mm2	White	0.013	0.60†	Same as above.
$\text{NaIO}_3$	mmm	White	0.004	0.000†	Same as above.
$\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$	—	White	0.018	—	Same as above.
$\text{KIO}_3$	mm2	White	2.4	4.0-8.0* 6.7†, 1.0‡	Same as above.
$\text{KIO}_3 \cdot 2\text{HIO}_3$	—	White	0.005	0.13*	Aqueous solutions by the gel method using $\text{KCl}$ and $\text{HIO}_3$ through silica gel.
$\text{Ca}(\text{IO}_3)_2$	—	White	0.009	—	Aqueous solutions by the gel method using $\text{CaCl}_2$ and $\text{HIO}_3$ .
$\text{Co}(\text{IO}_3)_2$	—	Purple	0.003	—	Slow evaporation of aqueous solution, also by the gel method using $\text{CoCl}_2$ and $\text{HIO}_3$ .
$\text{Cu}(\text{IO}_3)_2$	—	Green	0.005	—	Slow evaporation of $\text{NH}_4\text{OH}$ solution, also by the gel method using $\text{CuCl}_2$ and $\text{HIO}_3$ .
$\text{Cu}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$	—	Blue	0.008	—	Slow evaporation of $\text{NH}_4\text{OH}$ solution, also by the gel method using $\text{CuCl}_2$ and $\text{HIO}_3$ .
$\text{Zn}(\text{IO}_3)_2$	—	White	0.017	—	Gel method using $\text{ZnCl}_2$ and $\text{HIO}_3$ .
$\text{RbIO}_3$	mm2	White	1.2	2.7†	Slow evaporation of hot aqueous solution.
$\text{AgIO}_3$	—	White	0.033	—	Slow evaporation of $\text{NH}_4\text{OH}$ solution.
$\text{Cd}(\text{IO}_3)_2$	—	White	0.042	—	Slow evaporation of hot $\text{NH}_4\text{OH}$ solution.
$\text{CsIO}_3$	3m or 2	White	0.14	0.07†	Slow evaporation of hot aqueous solution.
$\text{NH}_4\text{H}_2\text{PO}_4$	$\bar{4}2m$	White	0.04	0.05†	Aqueous solution.
$\text{Ba}_2\text{NaNb}_5\text{O}_{15}$	mm2	White	2.6	2.6*, 6.7‡	Kyroupulos melt growth.
$\text{C}_{10}\text{H}_8\text{O}_3$	—	White	0.022	0.067‡	Slow evaporation from solutions of ethanol.
$\text{C}_9\text{H}_6\text{O}_2$	—	White	0.18	—	Slow evaporation from solutions of benzene and acetone.
$\text{C}_{14}\text{H}_{17}\text{NO}_2$	—	Yellow	0.4	0.6‡	Slow evaporation from solutions of benzene and acetone.

\*References 1 and 2.

†Reference 4.

‡Reference 5.

1.06  $\mu\text{m}$  and, as such, is a useful analytical tool to the nonlinear materials research program at NRL. Furthermore, an extension of this technique using a  $\text{CO}_2$  laser at 10.6  $\mu\text{m}$  should allow an initial evaluation of potential nonlinear materials for use in the infrared.

#### REFERENCES

1. S.K. Kurtz, and T.T. Perry, J. Appl. Physics 39, 3798 (1968)
2. S.K. Kurtz, IEEE J. Quantum Electronics QE-4, 578 (1968)
3. A. Graja, Phys. Stat. Sol. 27, K93 (1968); Acta Physica Polonica A37, 539 (1970)
4. J.G. Bergman, Jr., G.D. Boyd, A. Ashkin, and S.K. Kurtz, J. Appl. Physics 40, 2860 (1969)
5. M. Bass, D. Bua, R. Mozzi, and R.R. Monchamp, Appl. Physics Letters 15, 393 (1969)



## DOCUMENT CONTROL DATA - R &amp; D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
1. REPORT TITLE AN EVALUATION OF NONLINEAR OPTICAL MATERIALS BY THE SECOND-HARMONIC POWDER TECHNIQUE			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final report on one phase of the NRL Problem.			
5. AUTHOR(S) (First name, middle initial, last name) J.F. Giuliani, L.S. Goldberg and F. Von Batchelder			
6. REPORT DATE April 29, 1971		7a. TOTAL NO. OF PAGES 9	7b. NO. OF REFS 5
8a. CONTRACT OR GRANT NO. NRL Problem N01-22,501		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 7273	
b. PROJECT NO. ARPA Order 306, Amendment 15		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency Arlington, Va. 22209	
13. ABSTRACT The nonlinear optical properties of 21 crystalline materials, principally of the iodate family of compounds, were evaluated using the second-harmonic powder technique developed by Kurtz and Perry. By this method the second-harmonic radiation generated in a powdered sample by a laser at $1.06 \mu\text{m}$ was compared with a known reference, $\text{LiIO}_3$ , in this case. Of the materials tested, 12 have previously been reported on in the literature, and our results are in substantial agreement. $\text{KIO}_3$ and $\text{RbIO}_3$ are identified as having the most promise for crystal development effort. The remaining materials, observed for the first time, failed to exhibit appreciable second-harmonic intensity.			

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nonlinear optics Nonlinear crystals Second-harmonic generation						