SECOND-HARMONIC OF LIGHT GENERATION IN CRYSTAL POWDERS

By A. Graja

Institute of Physics, Polish Academy of Sciences, Poznań*

(Received June 10, 1969)

A method of SHG investigation in powders is proposed, presenting various advantages as compared to the classical method involving single crystal specimens: no high requirements are set regarding quality of the small crystals, and there is no need for tedious mechanical processing to obtain single crystal well-oriented plates. The powder method, though very simple, yields considerable information of the substance *i. e.* permitting to decide whether or not a matching direction exists, an advantage when searching for new materials in nonlinear optics. Also, the method allows determinations of mean values of nonlinear optical polarizability tensor components coherence length, anisotropy angle, coherence length in the matching direction for a given divergence of the laser beam, etc. The amount and importance of the information provided and the ease of sample preparation make this powder method highly commendable for the research of new optically nonlinear materials.

1. Introduction

The new light sources provided by lasers have currently made available light waves with an electric field strength of order 10^6-10^9 V/cm. In such intense fields, certain media exhibit their nonlinear optical properties, involving invalidation of the principle of superposition thus leading to an interaction between waves propagating simultaneously in the medium. A nonlinear medium transmitting an intense, coherent and monochromatic light wave becomes a source of radiation of other frequencies. In particular, this radiation can have a frequency twice that of the fundamental light wave, in which case one has the effect of *second-harmonic generation* of light (SHG) first observed by Franken and co-workers in 1961 [1]. In the numerous publications up to 1968, SHG was obtained recurring to crystal plates cut at appropriate orientation from a single crystal, involving considerable time and skill, but providing a high yield of the transduced frequencies and permitting a detailed study of SHG. The difficulty of the single crystal plate method has led to propose the powder method of SHG investigation [2].

The earliest theoretical and preliminary, experimental studies on SHG in powdered piezoelectric crystals are due to Filimonov and Suvorov [3], co-workers of Rez. By averageing

* Address: Instytut Fizyki PAN, Poznań, Grunwaldzka 6, Polska.

the second-harmonic flux over the grain size, they obtained, for crystals with a matching direction, a linear dependence of the second-harmonic power P_2 on the mean grain size, but no dependence of P_2 on d in crystals with no matching direction. Thier results were corroborated in a note [4] and paper [5] by Kurtz and Perry on the use of powder technique in assessing nonlinear optical materials.

As compared with the classical single crystal method, powder studies of SHG present important advantages. In the first place, it is sufficient to have at one's disposal quite small crystals of no high quality at all. Neither is there any longer a need for the tedious and by no means easy mechanical processing of plates appropriately oriented with regard to the axes of the single crystal. Despite its simplicity, the powder method yields a relatively large amount of information concerning the substance investigated.

2. Assumptions, and theoretical remarks

The theory of SHG in single crystals [6–11] is not directly applicable to specimens consisting of small crystalline grains. Simplifying assumptions [3, 5, 12] are necessary if one wishes to obtain a compact expression describing SHG in powders.

1°. We assume the grains to consist of a little crystal each, all being of the same size and oriented randomly.

2°. With respect to each grain we apply the theory of SHG valid for single crystals, but with respect to the sample as a whole we have to perform an averageing over angles.

3°. The second-harmonic power generated in the powder samples is the sum of the power generated in the grains (account taken of phase relations).

4°. Within a grain, the wave front of the fundamental wave is plane.

5°. The grains are in suspension in an immersion liquid.

6°. The number of grains traversed by a ray of the fundamental beam is large.

7°. The grains oriented in the matching direction present a grid behaving like a crystal plate cut in the matching direction.

With the above assumptions, it can be shown that the resultant second-harmonic intensity generated within the sample is equal to the sum of the contributions of the grains. Such a summation is justifiable since the phases of the waves generated in the various grains are mutually uncorrelated (provided the grain size exceeds the coherence length l_{coh} *i.e.* the path on traversing which the phase of an electromagnetic wave of frequency 2ω is shifted by π with respect to the phase of the nonlinear polarization wave). Since grain orientation is random, the expression describing SHG power in plates can be averaged over all angles. Quantities dependent on orientation are: the coherence length l_{coh}, and the mean values of elements of the nonlinear optical polarizability tensor $\chi_{ijk}^{2\omega}$. In crystals having a matching direction, the angular dependence of the coherence length plays the predominant part, whereas the dependence of $\chi_{ijk}^{2\omega}$ on orientation is of secondary importance.

At low birefringence and low dispersion, the coherence length in a direction differing by an angle $\pm\alpha$ from the matching direction is given by the formula [13, 14]:

$$(l_{\mathrm{coh}})_\alpha = \frac{\lambda}{4\alpha(n_2^e - n_2^0)\sin\Theta}, \tag{1}$$

with λ — the wavelength, n_2^0 and n_2^e the refractive indices of the ordinary and extraordinary second-harmonic (2ω) frequency light waves, Θ — the angle between the optical axis of the crystal and the matching direction (the latter being the direction in which the wave fronts of frequency ω and frequency 2ω propagate with equal velocity, thus satisfying the equation $\boldsymbol{k}_2 = 2\boldsymbol{k}_1$).

Perry and Kurtz [5], on inserting this expression into the general formula for the second-harmonic intensity $I_{\text{ext}}^{2\omega}$ outside the crystal as a function of the parameters of the fundamental beam and on integrating over all angles, obtained:

$$I_{\text{ext}}^{2\omega} = \frac{32\pi}{c}\left[\frac{64 I_{\text{ext}}^{\omega}}{\lambda(n_1+1)^2(n_2+1)}\right]^2 (\chi_{PM}^{2\omega})^2 \frac{\pi^2}{4} L\Gamma_{PM}, \tag{2}$$

with the notation $\Gamma_{PM} = \dfrac{\pi \sin\Theta}{\gamma}$ and $\gamma = \dfrac{\omega n_1^0}{c}\sin\beta$, n_1 and n_2 the refractive indices for frequencies ω and 2ω respectively; L the thickness of the sample; I_{ext}^{ω} the intensity of the fundamental beam of frequency ω; $\chi_{PM}^{2\omega}$ those elements of the tensor $\chi_{ijk}^{2\omega}$, or their combinations, which are active in SHG in the matching direction; β the anisotropy angle of the crystal *i.e.* the angle $(\widehat{\boldsymbol{S}_1^0\,\boldsymbol{S}_2^e})$ between the directions of rays $\boldsymbol{S}_1^0$ and $\boldsymbol{S}_2^e$ having respectively the fundamental frequency ω and the second-harmonic frequency 2ω or, in the other words, the angle between the matching direction of phase velocities (for which $\boldsymbol{k}_2^e = 2\boldsymbol{k}_1^0$) and the direction of $\boldsymbol{S}_2^e$ ($\widehat{\boldsymbol{k}_2^e\,\boldsymbol{S}_2^e} = \widehat{\boldsymbol{k}_1^0\,\boldsymbol{S}_2^e}$). A geometrical interpretation of the anisotropy angle β is given in Fig. 1, where it is seen to be definable also as the angle subtended by the normals to the surfaces of refractive indices at their point of intersection, The anisotropy angle β represents an important parameter characterizing the nonlinear properties of a crystal,

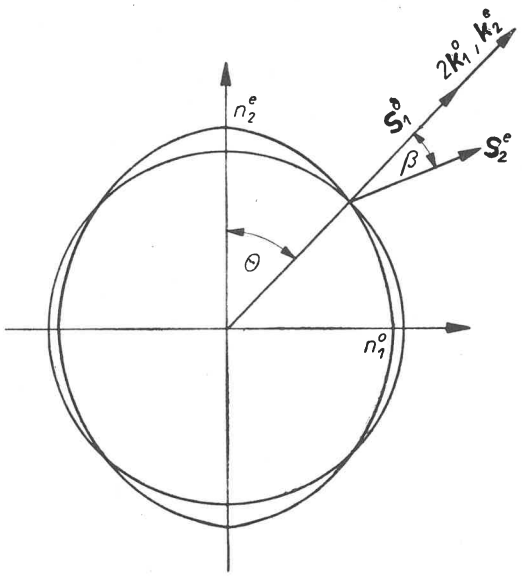

Fig. 1. Cross-section through the surfaces of refractive indices n_1^0 and n_2^e, showing the matching angle Θ and anisotropy angle β

since it difines the angular width of the principal maximum of second-harmonic power generated in the matching direction.

An analysis of Eq. (2) shows that in the case of large grains $\left(d \gg \frac{\Gamma_{PM}}{\sin \Theta}\right)$ the second-harmonic intensity $I_{\text{ext}}^{2\omega}$ does not depend on the mean grain size d, whereas in that of small grains $\left(d \ll \frac{\Gamma_{PM}}{\sin \Theta}\right)$ a linear dependence of $I_{\text{ext}}^{2\omega}$ on d can be expected tohold.

The powder method is moreover well-adapted for studying SHG caused by divergent beams [12]. Indeed, a sample containing a sufficiently large number of grains will present some number of crystallites oriented approximately in the matching direction. Thus, their matching directions will lie within body angles lesser than the divergence angle α of the laser beam. The set of these specified grains can be considered as kind of grid, behaving macroscopically as a crystal plate (reduced in surface) cut in the matching direction. From the geometrical viewpoint the probability of finding a grain oriented close to the matching direction is (for small angles α) directly proportional to α. As a consequence, the angular power distribution of SHG in the powder sample is obtained by recurring to the distribution formula for a crystal plate and taking into account the probability of finding a grain oriented close to matching direction. SHG in plates due to a divergent beam was studied by the authors of Refs [14] and [16] recurring to parabolic equations and resulting in the following formula for the angular distribution of SHG intensity for one-dimensional interaction in a single crystal plate:

$$I^{2\omega}(\alpha, \varphi, L) = A \frac{\sin^2 k_0 \beta \alpha L}{(k_0 \beta \alpha L)^2}, \tag{3}$$

where k_0 and A are constants, and the remaining symbols are as above.

Consequently, the second-harmonic power generated in a sample consisting of powdered crystals can be expressed as:

$$I^{2\omega} = B' \frac{\sin^2 k_0 \beta \alpha L}{(k_0 \beta \alpha L)^2} \alpha = B \frac{\sin^2 k_0 \beta \alpha L}{k_0 \beta \alpha L}. \tag{4}$$

This equation has the shape of the function $\frac{\sin^2 x}{x}$, instead of $\frac{\sin^2 x}{x^2}$ as was the case for the single crystal [8, 10, 11, 15, 16]. The two functions are similar in shape, but differ as to the position of the central maximum, which undergoes a shift towards angles $x > 0$, and lies approximately in the point $x = 1{,}19$ rd. Other maxima are near $x_{\max} = (2k+1)\pi/2$, whereas minima occur at $x_{\min} = k\pi$. The first maximum contains but 63 per cent of the SHG power from powder samples; the consecutive maxima contain respectively about 18, 11 and 6 per cent of the total second-harmonic power. Grains having an orientation strongly different from the matching direction contribute to SHG in a manner which depends moreover on the divergence α of the fundamental beam. This contribution is described by a periodic function with a period of the order of 10^{-6} rd, which is experimentally imperceptible but is apparent as a constant background effect independent of the fundamental beam diver-

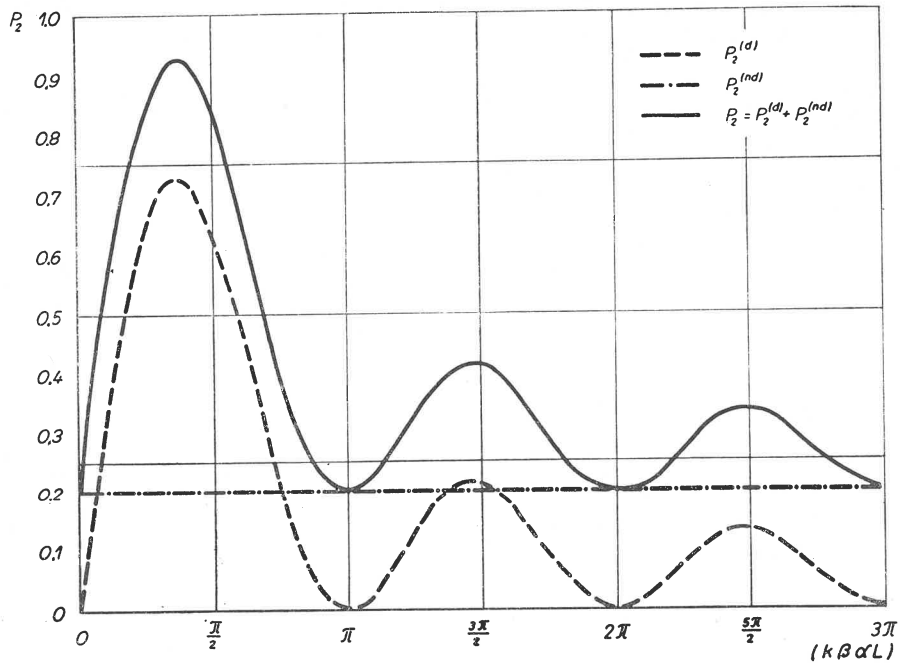

Fig. 2. Contribution of matched grains P_2^d, non-mathed grains P_2^{nd}, and resultant second-harmonic power P_2. Ordinates: Second-harmonic power in relative units. Abscissae: Divergence of the laser beam in degrees of the arc

gence α. This is shown diagrammatically in Fig. 2, where the contribution from matched grains is plotted as curve P_2^d, that of non-matched grains as curve P_2^{nd}, and the resultant SHG power as curve P_2; the ratio P_2^{nd}/P_2^d is seen to depend on α.

3. Results of measurements, and interpretation

SHG of light in powdered crystals was studied with standard equipment [1, 3, 8, 10, 12, 17], but using a sample of calibrated, finely powdered crystal substance in place of an oriented single crystal. A block diagram of the device is shown in Fig. 3.

The measuring system consisted essentially of a ruby laser *1–3* emitting a beam of coherent, monochromatic light of wavelength $\lambda = 694{,}3$ nm and power about 3 kW, operating [18] in normal circuit and hence having a relatively long action duration (about 200 μs). The beam was incident upon a beam splitter *4* acting simultaneously as red filter eliminating some negligible admixture of scattered UV from the xenon flash tube. The portion of the beam reflected from the plate was incident upon the photomultiplier energy meter [19] *11*, *12*, *18*, *19*, and moreover was rendered accessible to observation and photography on an oscillograph screen *11*, *12*, *20*. The principal portion of the beam was transmitted through the plate *4* and, after focussing with the lense *3*, reached the sample *6*. The second-harmonic generated in the sample was separated from the very intense laser radiation by means of

filters *7* and a VSU1 monochromator *8*. Next followed a photomultiplier *9* permitting to observe and take picture of the SHG signal on the oscillograph screen *20* or to plot the energy of SHG with a recording device *18*, *19*.

The sample was prepared as follows: single crystals of the substance investigated were ground in a mortar and then passed throug a set of 10 sieves of known aperture. In this way, 10 samples of grain size ranging from 0.05 to 0.49 mm were obtained. In some experiments, instead of grinding single crystals in a mortar, a special technology of crystal growing was employed, namely so-called fast crystallization at sudden cooling of the saturated solution,

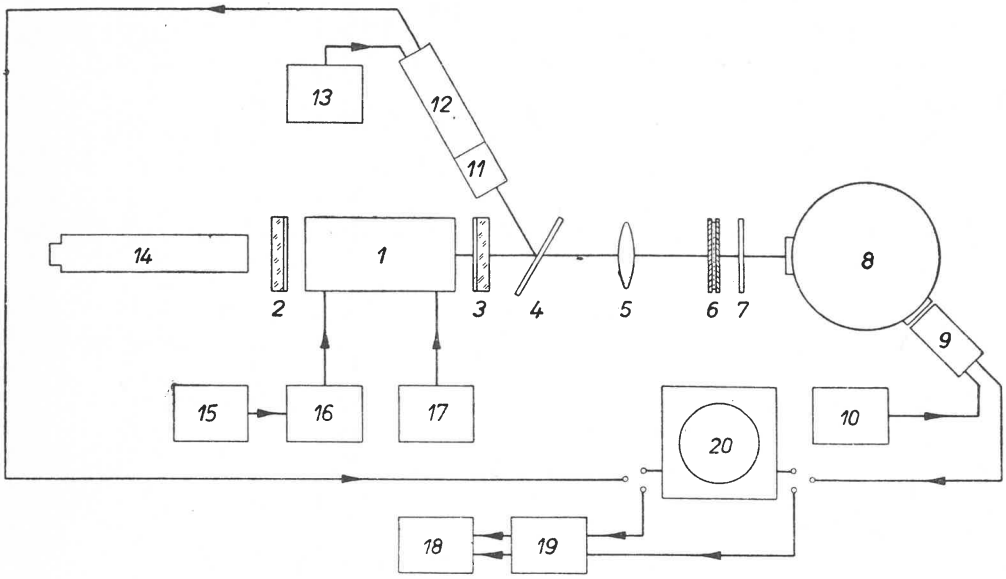

Fig. 3. Block diagram of equipment for studying SHG in powders

yielding very fine crystal grains. The powder grown by the latter method was washed and dried, and then made to pass the sieves. The powders were mixed with the immersion liquid at a well-defined ratio and placed between two microscope glasses, yielding a thin layer of approximately constant thickness and dense grain packing.

SHG power was measured from samples prepared by either procedure. In the case of small grains (granulation < 0.15 mm), the SHG power was found not to depend on the technology recurred to in preparing the powder. In that of larger grains, a dispersion of the results appeared due to the presence of crystallites consisting of several little single crystals sticking together. This was confirmed by microscopic observation, which revealed crystallites consisting of two, three or even more grains in the samples. Obviously, the second-harmonic power generated in such an agglomerate is not the same as that generated in a single grain of equivalent size. The presence of crystallites was responsible for the occurrence of "saturation" in the dependence of the SHG power on the grain size. The shape of this function was studied for various crystals and various divergences of the laser beam. Figs. 4 — 6 show the graphs as obtained for ADP crystals grown by the method of fast crystallization. The

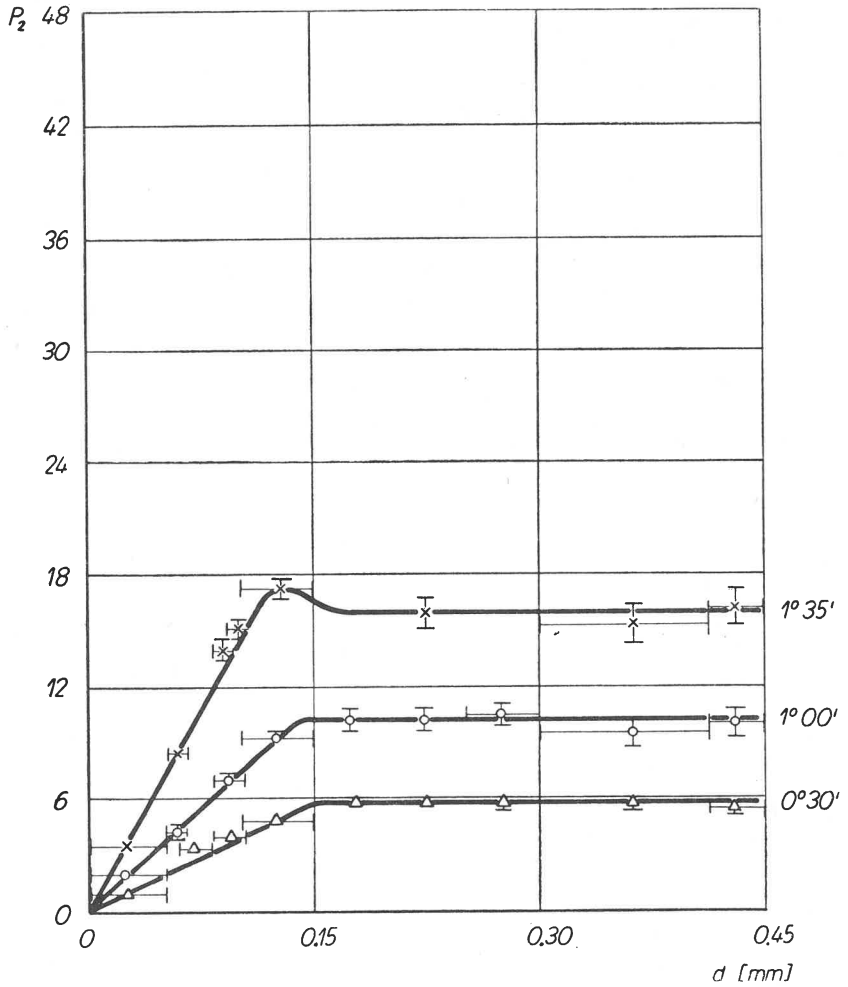

Fig. 4. Second-harmonic power *versus* the size of ADP crystal grains obtained by fast crystallization. Divergences of the laser beam: 0°30′; 1°00′; 1°35′. Ordinates: Second-harmonic power in relative units. Abscissae: Mean grain size in mm

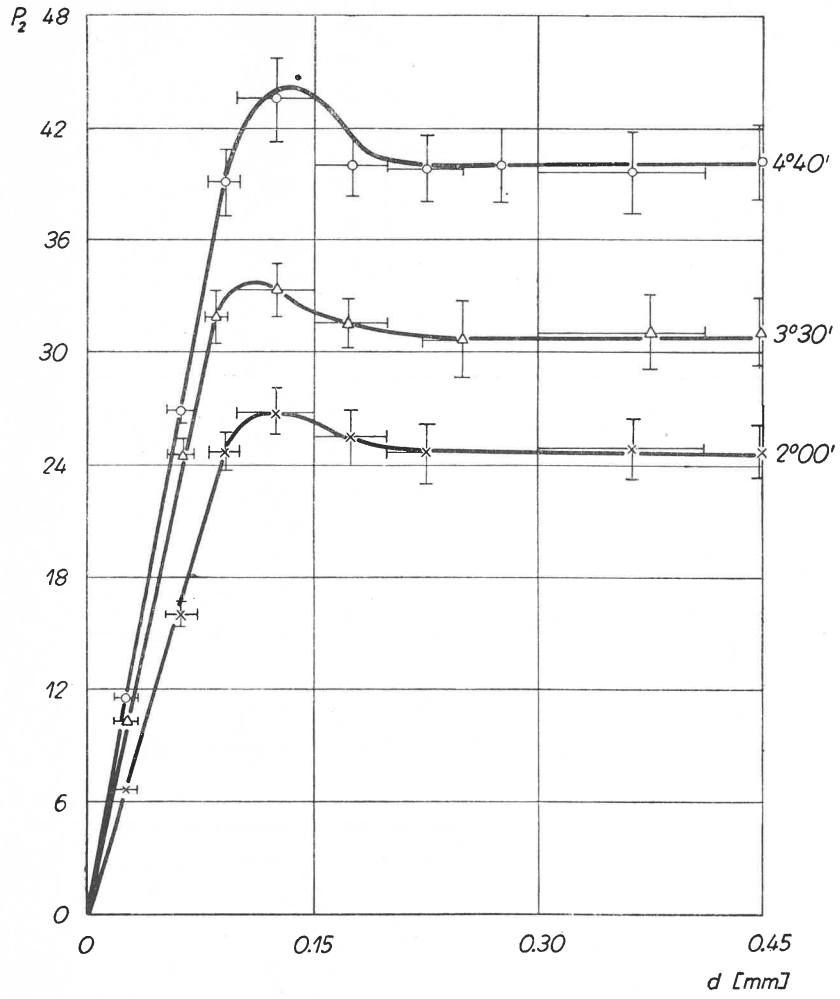

Fig. 5. Second-harmonic power *versus* the size of ADP crystal grains obtained by fast crystallization. Divergences of the laser beam: 2°00′; 3°30′; 4°40′. Ordinates: Second-harmonic power in relative units. Abscissae: Mean grain size in mm

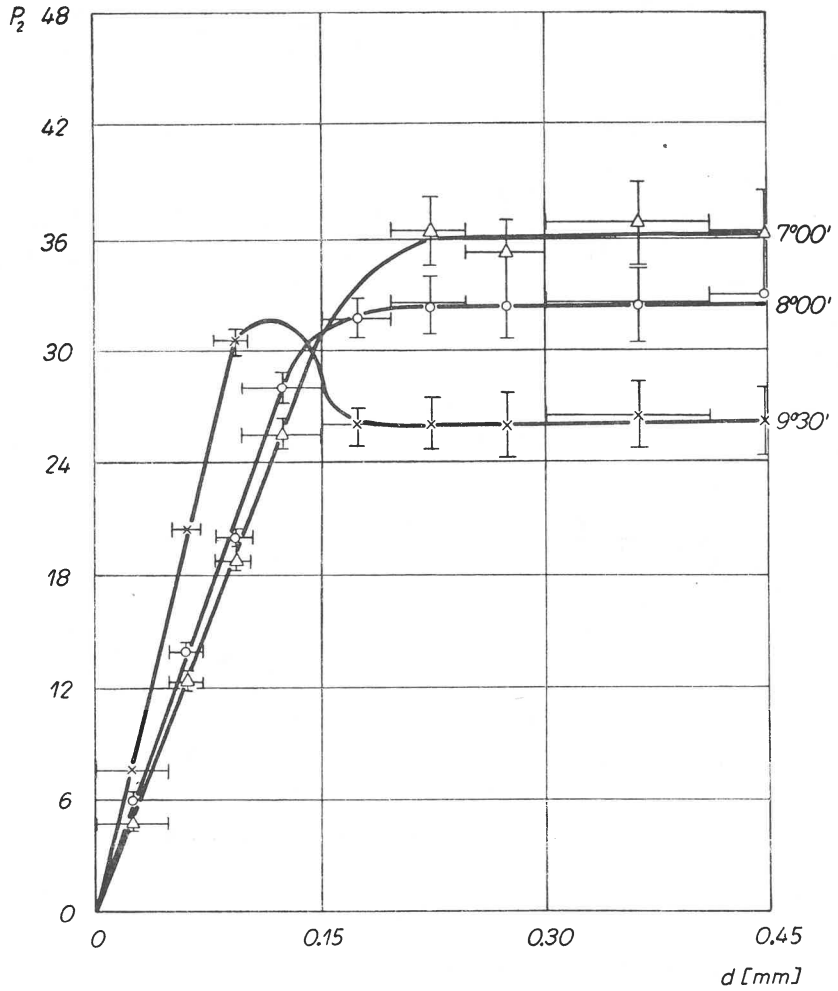

Fig. 6. Second-harmonic power *versus* the size of ADP crystal grains obtained by fast crystallization. Divergences of the laser beam: 7°00′; 8°00′; 9°30′. Ordinates: Second-harmonic power in relative units. Abscissae: Mean grain size in mm

SHG power is seen to increase linearly with increasing mean dimensions of the grains only in the range of small granulation values ($d \leqslant 0.1$ mm). This is in agreement with the theoretical predictions. For larger granulation values in the range $0.1 \leqslant d \leqslant 0.2$ mm, the graph of $P_2(d)$ deviates from linearity due to the fact that, beside the single grains, double and even triple grains begin to appear, each of these species contributing a second-harmonic power proportional to the mean dimensions of the grains forming the crystallite. For large granulation values of $d > 0.20$ mm, the SHG power ceases to depend on the grain size. This is hardly surprising, as the large grains consist almost exclusively of little crystals having mean dimensions of about 0.15 mm. As a result, the SHG power takes the value it should have for grains of about 0.15 mm.

"Saturation" of this kind does not occur in samples made of powder obtained by grinding crystals in a mortar. Nevertheless, according to the theoretical calculations of Kurtz and Perry [5], "saturration" has to appear if the mean dimensions of the grains exceed the coherence length for the laser beam divergence. This effect was indeed found in an ADP sample for a laser beam of divergence 58° (Fig. 7).

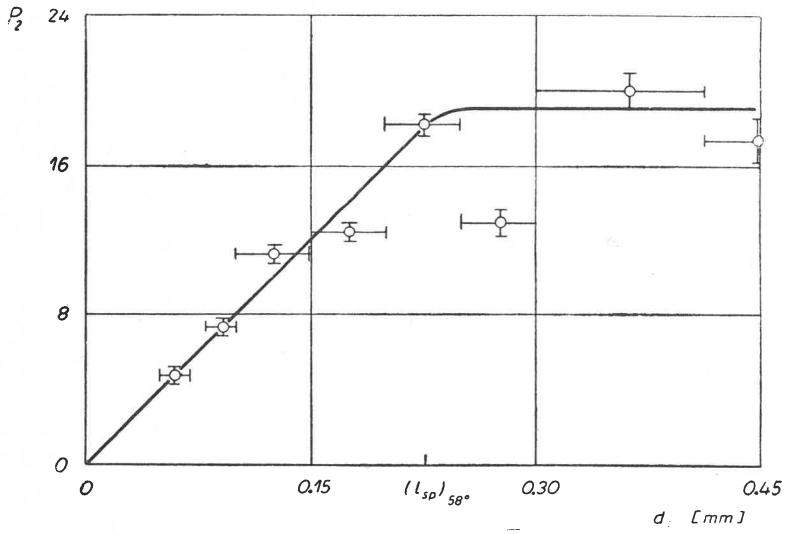

Fig. 7. Second-harmonic power *versus* the size of ADP crystal grains ground in a mortar. Divergence of the laser beam 58°. Ordinates: Second-harmonic power in relative units. Abscissae: Mean grain size in mm

The experimental date served for calculating the coherence length at divergence 58°, resulting in a value of 0.25 mm, whereas the theoretical value was 0.225 mm.

Figs. 8 and 9 show date from similar measurements in RDP samples. The power P_2 increases linearly up to dimensions of about 0.25 mm. The curves run similarly as in ADP, there are only some numerical differences due to different crystallization conditions of RDP as compared with ADP.

Figs 10, 11 and 12 concern ADP crystals with admixtures of chromium ion. P_2 grows linearly only in grains of less than about 0.11 mm, upward of which "saturation" is observed.

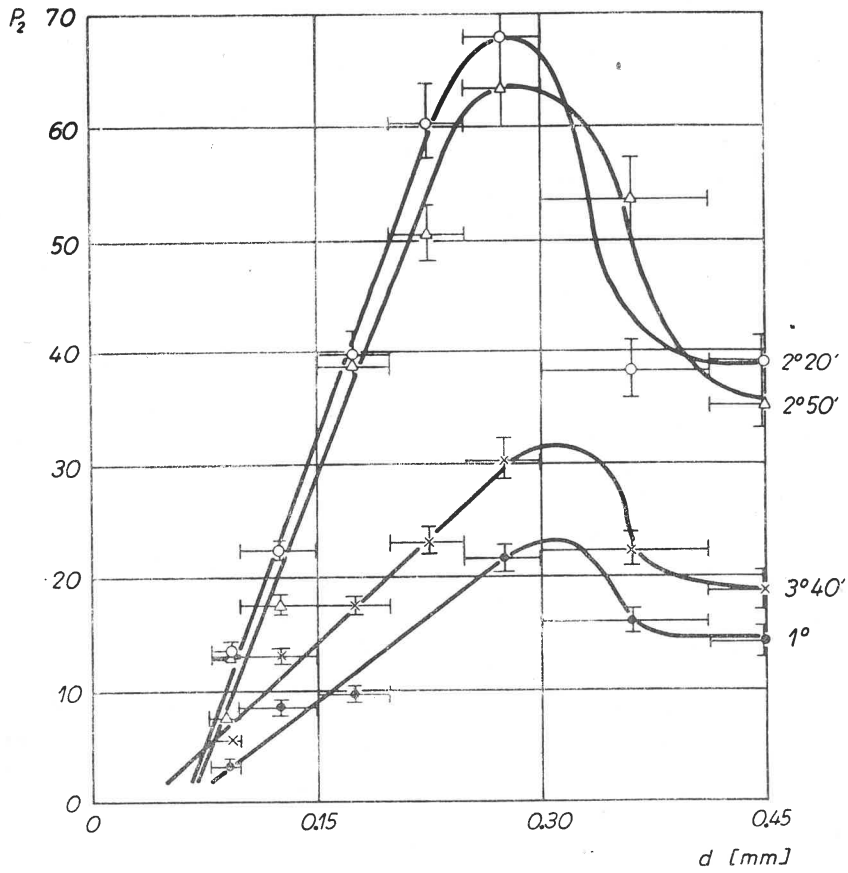

Fig. 8. Second-harmonic power *versus* the size of RDP crystal grains obtained by fast crystallization. Divergences of the laser beam: 1°00′; 2°20′; 2°50′; 3°40′. Ordinates: Second-harmonic power in relative units. Abscissae: Mean grain size in mm

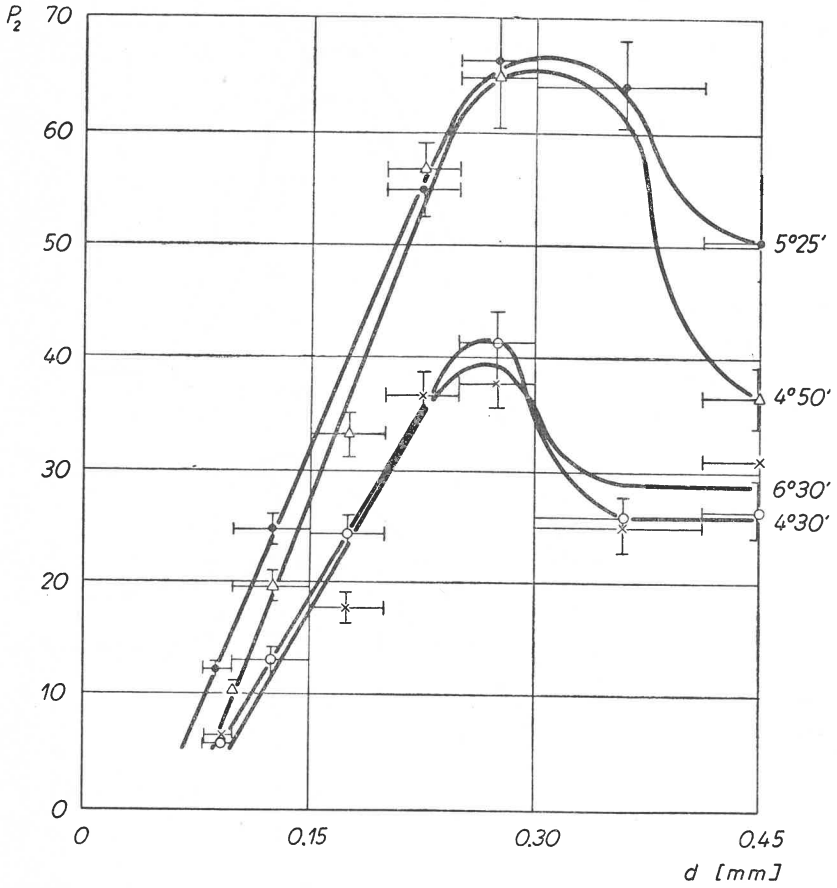

Fig. 9. Second-harmonic power *versus* the size of RDP crystal grains obtained by fast crystallization. Divergences of the laser beam: 4°30′; 4°50′; 5°25′; 6°30′. Ordinates: Second-harmonic power in relative units. Abscissae: Mean grain size in mm

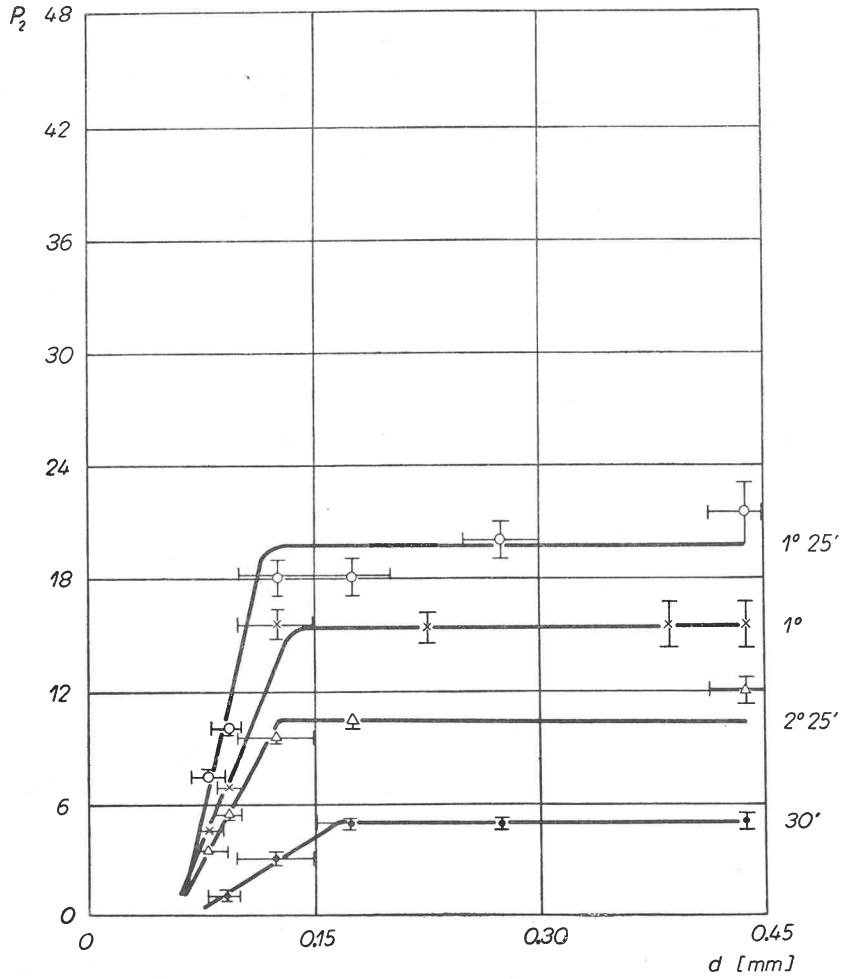

Fig. 10. Second-harmonic power *versus* the size of ADP: Cr^{3+} crystal grains obtained by fast crystallization. Divergences of the laser beam: 0°30′; 1°00′; 1°25′; 2°25′. Ordinates: Second-harmonic power in relative units. Abscissae: Mean grain size in mm

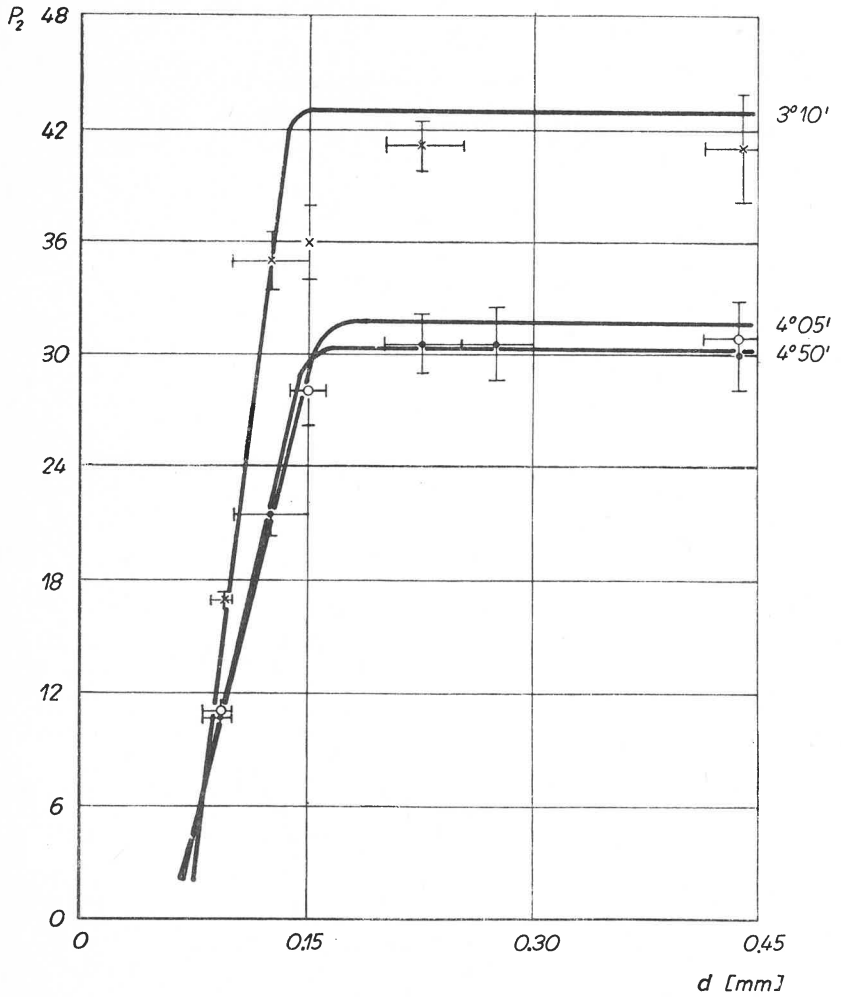

Fig. 11. Second-harmonic power *versus* the size of ADP: Cr^{3+} crystal grains obtained by fast crystallization. Divergences of the laser beam 3°10′; 4°05′; 4°50′; Ordinates: Second-harmonic power in relative units. Abscissae: Mean grain size in mm

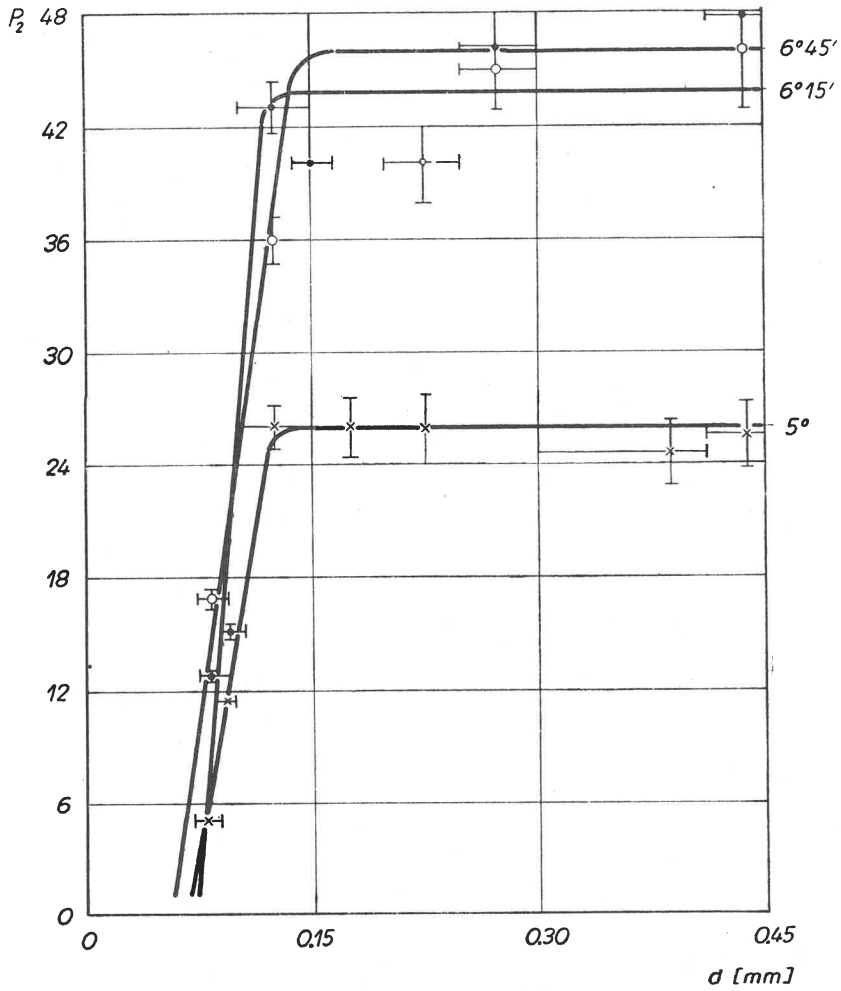

Fig. 12. Second-harmonic power *versus* the size of ADP:Cr^{3+} crystal grains obtained by fast crystallization. Divergences of the laser beam: 5°00′; 6°15′; 6°45′. Ordinates: Second-harmonic power in relative units. Abscissae: Mean grain size in mm

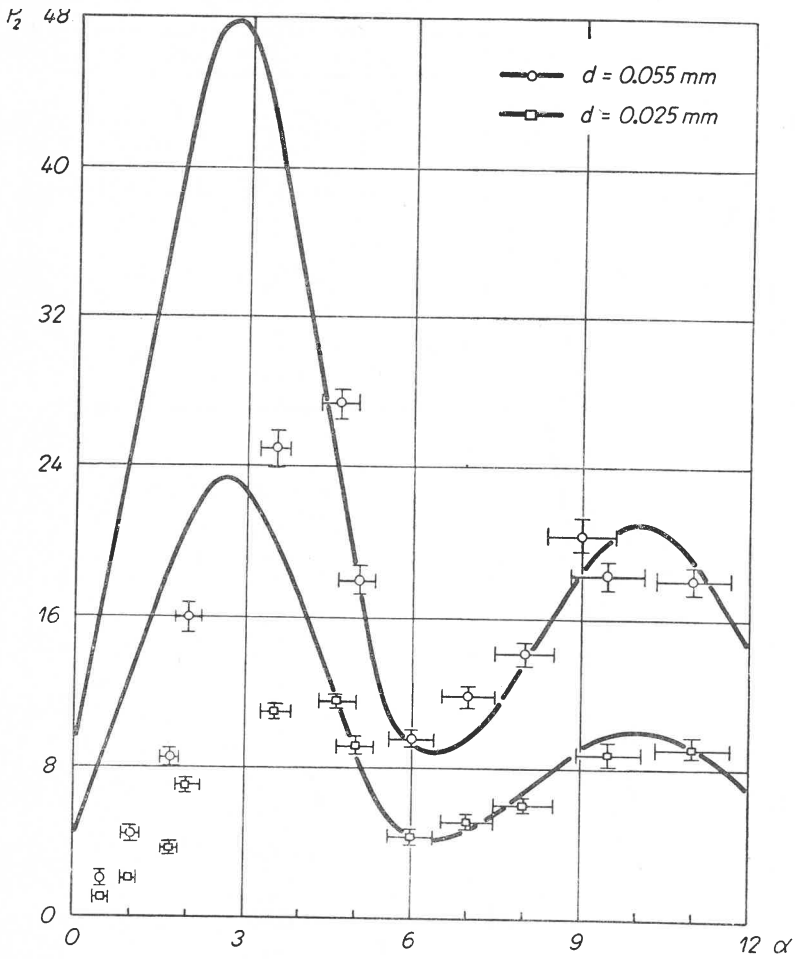

Fig. 13. Second-harmonic power *versus* the laser beam divergence, for ADP powder of grain size 0.055 mm and 0.025 mm. Ordinates: Second-harmonic power in relative units. Abscissae: Divergence of the laser beam in degrees of the arc

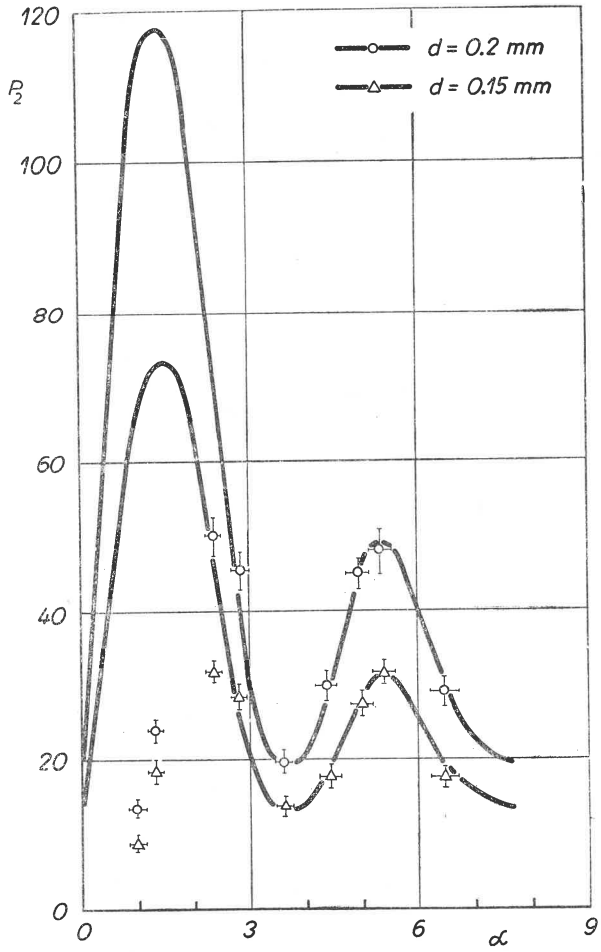

Fig. 14. Second-harmonic power *versus* the laser beam divergence, for RDP powder of grain size 0.15 mm and 0.2 mm. Ordinates: Second-harmonic power in relative units. Abscissae: Divergence of the laser beam in degrees of the arc

An analysis of the conditions admitting of such relationships showed that these conditions favoured the formation of grains smaller than 0.11 mm but not larger, so that the large crystallites consisted of just such grains.

Also, SHG power was studied as a function of the laser beam divergence (Figs 13, 14 and 15 for ADP powder, RDP and ADP : Cr^{3+}, respectively, where the theoretical curves have been plotted from Eq. (4) with the anisotropy angles β from the literature [20, 21],

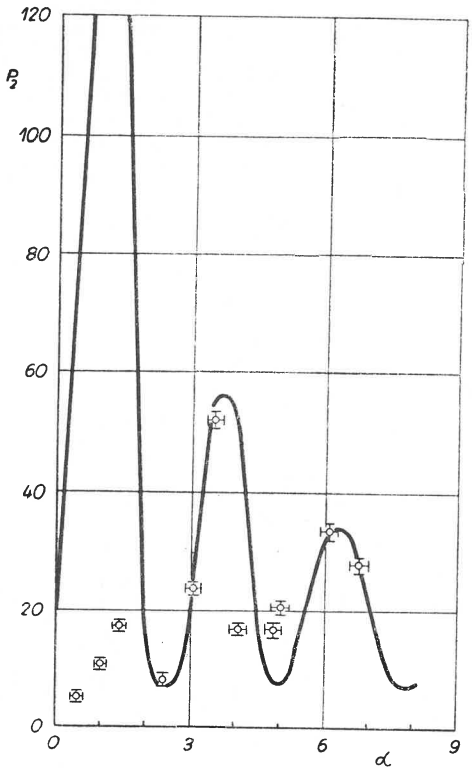

Fig. 15. Second-harmonic power *versus* the laser beam divergence, for ADP: Cr^{3+} powder of grain size 0.05 mm. Ordinates: Second-harmonic power in relative units. Abscissae: Divergence of the laser beam in degrees of the arc

and the dots are experimental results). The theoretical curves of Figs 13–15 render the experimental situation satisfactorily only for the case of rather strongly divergent beams. Hence, the assumptions made when deriving Eq. (4) cease to be correct at low divergences of the beam, when the coherence length becomes much larger than the mean grain size, and consequently the assumption of the absence of phase correlations between waves from the various grains no longer holds. From the positions of the consecutive maxima on the experimental $P_2(\alpha)$ curves, the anisotropy angle of the crystal can be calculated, leading to $\beta = 1°50'$ in ADP, 3°15′ in RDP, and 4°55′ in ADP : Cr^{3+}. Thus, an admixture of chromium ion causes an increase of the anisotropy angle equivalent to a narrowing of the angular region

(section) participating in SHG while providing for equality of the respective phase velocities.

Measurements were made of the second-harmonic power generated in a powder sample under the influence of sections of a laser beam of well-defined power and divergence. In limiting the beam, diaphragms with apertures of 1.3 and 0.4 mm were used. The sample was an ADP powder of 0.43 mm granulation. This experiment showed that a non-matched grain contributes about 2 relative units whereas a grain oriented in the matching direction

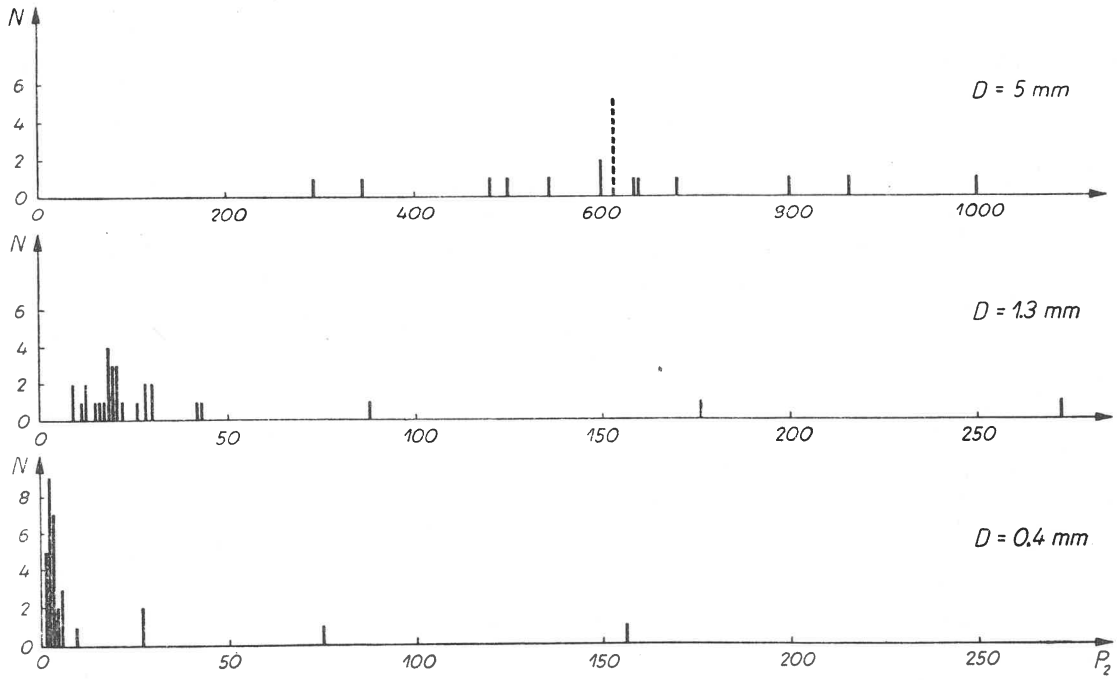

Fig. 16. Diagram showing the number of recurrences of second-harmonic power values. Ordinates: Number of recurrence of a measured value. Abscissae: Second-harmonic power in relative units

yields about 200 relative units. Thus, with known number of grain and probability of finding a matched grain, calculation for the sample without diaphragms led to predict a signal of 608 such units. The mean value from some 20 measurements was 612 relative units. This is shown in Fig. 16, where the recurrence distribution of experimental results is normal, showing that mean values have to be taken in order to eliminate the effect of random grain distribution in the sample and energy fluctuations in the beam.

4. Conclusions

The above proposed method of SHG studies in piezoelectric crystal powders permits to establish whether a crystal presents the conditions for a matching direction. By comparing the SHG power from the powder under investigation and the SHG power from a standard

sample, one can determine the mean values of the nonlinear optical polarizability tensor components. These data, together with information as to the presence or lack of a matching direction, make possible a classification of any crystal with regard to its utility in nonlinear optics. Measurements like those described above enable to determine with relative ease such characteristic parameters as the coherence length l_{coh}, the coherence length in the matching direction $(l_{coh})_{\alpha}$, the anisotropy angle β, and so forth. The results are in good numerical agreement with the literature date for single crystals, whereas the powder method is the more convenient one. SHG investigations in powders are particularly well adapted to the search for new nonlinear optical materials. Accordingly, beside the well-known ADP, KDP, RDP, ADA, KDA and similar substances, investigation was extended to the novel pentaborate group, as yet not utilized in nonlinear optics. Ammonium pentaborate was found to present a matching direction as well a relatively high frequency tranducing efficiency. Its greatest advantage can be said to reside in its applicability to fast and standardized evaluations of optically nonlinear materials, and the method may yet prove useful in other branches of research.

The author wishes to thank Docent Dr J. Małecki for his guidance throughout and inspiring discussions of the results of this investigation.

Thanks are due to Dr B. Hilczer, W. Kuczyński, M. Sci., L. Szczepańska, M. Sci., and Mrs A. Stelmaszyk for their valuable cooperation.

REFERENCES

[1] P. A. Franken, A. E. Hill, C. W. Peters, G. Weinreich, *Phys. Rev. Letters*, **7**, 118 (1961).
[2] I. S. Rez, V. S. Suvorov, (private communication).
[3] A. A. Filimonov, V. S. Suvorov, (in press).
[4] A. Graja, *Phys. Status Solidi*, **27**, K93 (1968).
[5] S. K. Kurtz, T. T. Perry, *J. Appl. Phys.*, **39**, 3798 (1968).
[6] J. A. Armstrong, N. Bloembergen, J. Ducuing, P. S. Pershan, *Phys. Rev.*, **127**, 1918 (1962).
[7] N. Bloembergen, *Proc. IEEE*, **51**, 124 (1963).
[8] P. A. Franken, J. F. Ward, *Rev. Mod. Phys.*, **35**, 23 (1963).
[9] D. A. Kleinman, *Phys. Rev.*, **128**, 1761 (1962).
[10] S. A. Akhmanov, R. V. Khokhlov, *Problemy nyelineynoy optiki*, Moskva 1964.
[11] N. Bloembergen, *Nonlinear Optics*, New York 1965.
[12] A. Graja, *Report at the IV-th Sympozium on Nonlinear Optics at Kiev*, October 1968.
[13] A. Ashkin, G. D. Boyd, J. M. Dziedzic, *Phys. Rev. Letters*, **11**, 14 (1963).
[14] S. A. Akhmanov, A. I. Kovrigin, R. V. Khokhlov, O. N. Chunayev *Zh. Exper. Teor. Fiz.*, **45**, 1336 (1963).
[15] P. D. Maker, R. W. Terhune, M. Nisenoff, C. M. Savage, *Phys. Rev. Letters*, **8**, 21 (1962).
[16] A. I. Kovrigin, N. K. Podsotskaya, A. P. Sukhorukov, *Proceedings of the II-nd Symposium on Nonlinear Optics at Novosibirsk*, 1968, p. 393.
[17] A. Graja, *Postępy Fizyki*, **18**, 539 (1967).
[18] F. Kaczmarek, A. Graja, A. Drobnik, A. Planner, *Fiz. Diel. i Radiospektr.*, **4**, 171 (1967).
[19] A. Graja, W. Kuczyński, *Fiz. Diel. i Radiospektr.*, **1**, 155 (1969).
[20] A. I. Kovrigin, *Doctor's Thesis*, Moscow State University, Moskov 1966.
[21] I. S. Rez, *Uspekhi Fiz. Nauk*, **93**, 633 (1967).