SOVIET PHYSICS JETP VOLUME 29, NUMBER 5 NOVEMBER, 1969

INVESTIGATION OF THE GENERATION OF A SECOND HARMONIC OF LASER RADIATION IN FINELY DISPERSED CRYSTALLINE MEDIA

A. A. FILIMONOV, V. S. SUVOROV, and I. S. REZ

Submitted December 20, 1968

Zh. Eksp. Teor. Fiz. 56, 1519–1523 (May, 1969)

An investigation was made of the generation of a second harmonic of a ruby laser in powders of the following crystals: ADP ($NH_4H_2PO_4$), KDP (KH_2PO_4), RDP (RbH_2PO_4), RDA (RbH_2AsO_4), potassium tartrate ($K_2C_4H_4O_6\cdot\frac{1}{2}H_2O$), potassium-lithium sulfate ($KLiSO_4$), and quartz. It was found that the phase matching could be detected by measuring the power of the second harmonic as a function of the average grain size. A comparison was made of the experimental data obtained for powders and single crystals of ADP, KDP, RDP, and DKDP along the phase-matching direction. The calculated and experimental data for ADP and quartz were compared.

In view of the considerable recent interest in the preparation of new nonlinear optical crystals[1,2] and the difficulties encountered in the synthesis and growth of relatively large crystals of optical quality, even on research scale, it seemed highly desirable to carry out a study of powders of these substances.

A rigorous approach to the problem of the propagation of waves and the generation of harmonics in a nonlinear randomly inhomogeneous medium is very complex. Several papers have dealt with special cases; for example, Bespalov[3] considered a random distribution of the phase-matching directions in the planar case. Experimental data were reported in [4,5] on the observation of harmonics in powders of some crystals.

The present paper reports a study of the generation of the second harmonic, including the influence of the random distribution of powder grains in a plane perpendicular to the direction of radiation of the fundamental frequency.

We shall consider an assembly of a large number of randomly distributed fine crystals of known symmetry, whose size varies at random from l_1 to l_2, and we shall consider only one layer of grains along the direction of propagation of a wave. We shall describe the orientation of grains by randomly varying angles φ, ψ, and θ, shown in Fig. 1.

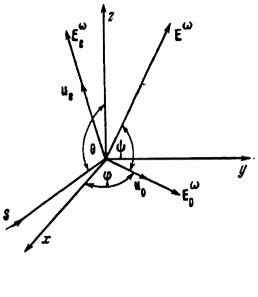

FIG. 1. Selection of angles representing the orientation of a crystal relative to the direction of the fundamental-frequency ray: a) $0 \leqslant \theta \leqslant \pi$ is the angle between the direction of the ray and z axis; b) $0 \leqslant \psi \leqslant 2\pi$ is the angle between E^ω and E_0^ω; c) $0 \leqslant \varphi \leqslant 2\pi$ is the angle which determines the projections of the vector E_0^ω along the x and y axes; u_0 and u_e are unit vectors along the direction of vibrations of the fundamental-frequency electric vector in a crystal for the ordinary (o) and extraordinary (e) waves. S is the direction of the ray.

Two fundamental-frequency waves, E_0^ω and E_e^ω, are propagated in each birefringent grain: these waves are polarized along two mutually perpendicular planes, giving rise to a nonlinear polarization at a frequency 2ω:[6]

$$P_i^{2\omega} = \chi_{ijk}E_{oj}^\omega E_{ok}^\omega + \chi_{ijk}E_{ej}^\omega E_{ek}^\omega + \chi_{ijk}E_{oj}^\omega E_{ek}^\omega, \tag{1}$$

where o and e are, respectively, the indices of interacting ordinary and extraordinary waves of frequency ω; i, j, k = 1, 2, 3; summation is carried out in the case of repeated indices.

Using the expression in [7] for the second-harmonic flux, we can find its average value

$$S^{2\omega} = \int_{l_1}^{l_2}\int_{\varphi_1}^{\varphi_2}\int_{\psi_1}^{\psi_2}\int_{\theta_1}^{\theta_2} 2\pi c \frac{\sin^2(\omega l \Delta n/c)}{n_{2\omega}\Delta n^2}(\mathbf{P}^{2\omega}\cdot\mathbf{u})\cdot f(l)f(\varphi)f(\psi)f(\theta)\,dl\,d\varphi\,d\psi\,d\theta, \tag{2}$$

where ω is the frequency of the fundamental radiation; l is the grain size; $n_{2\omega} = n_{2\omega}(\theta)$ is the refractive index at the frequency 2ω (for the ordinary wave, $n_{2\omega}$ = const); $\Delta n = \Delta n(\theta)$ is the difference between the refractive indices of the fundamental and second-harmonic frequencies (for the ordinary wave, Δn = const); $\mathbf{P}^{2\omega}\cdot\mathbf{u} = F(\varphi, \psi, \theta)$ depends on the particular type of crystal symmetry; $\mathbf{P}^{2\omega}$ is the nonlinear polarization vector at the frequency 2ω; $\mathbf{u}$ is the direction of the electric vector of the waves of frequency ω in the crystal; $f(l) = 1/(l_2 - l_1)$, $f(\varphi) = 1/2\pi$, $f(\psi) = 1/2$, $f(\theta) = 1/2 \sin\theta$ are the probability densities. The dependence of the refractive index on φ must be allowed for in Eq. (2) in the case of optically biaxial crystals.

In the experimental investigation, we used the apparatus shown in Fig. 2. The effects of the instability of

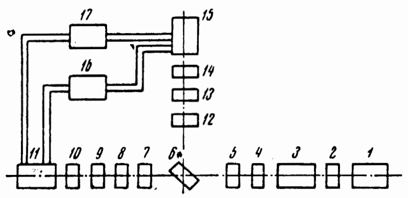

FIG. 2. Block diagram of the apparatus used to measure the second harmonic generated in finely dispersed samples. 1) Collimator; 2) mirror; 3) pulsed ruby laser; 4) mirror; 5) red optical filter; 6) rotatable plate; 7) red optical filter; 8) investigated sample; 9) step attenuator; 10) monochromator; 11) photomultiplier; 12) red optical filter; 13) standard sample; 14) set of violet filters; 15) photomultiplier; 16) double peak voltmeter; 17) power-pack.

the radiation were eliminated by the use of a comparison arm. A finely dispersed sample of RDP, immersed in an acrylic adhesive, was used as the standard crystal. Signals from photoelectric multipliers were integrated and applied to a double peak voltmeter of the DPV-1 type. The use of a peak voltmeter with a signal memory increased considerably the reliability of readings and reduced the time required to obtain the results, as compared with the oscillographic method.

The samples used in the measurements were prepared as follows. A vibrating sieve separated the powder to be investigated into fractions of grain size 50–100 μ, 100–145 μ, 145–220 μ, 220–390 μ. A batch of the powder was placed on a quartz substrate using a measure of 0.09 cm^3 volume, two drops of the immersion liquid were added, the liquid was mixed thoroughly with the crystals, and then a quartz cover was pressed tightly against the substrate.

The ratio of the volumes of the immersion liquid and the substance under investigation was selected so as to ensure a uniform distribution of grains in the form of a monolayer. The immersion liquids were silicone oils with refractive indices from 1.42 to 1.57, which were transparent at the fundamental and the second-harmonic wavelengths.

The optical transmission of the samples was checked by using a QR-50 spectrophotometer; it was 90% for $\lambda = 6943$ Å and 75% for $\lambda = 3472$ Å.

The power of the second harmonic was measured in relative units. The reference unit was the power of the second harmonic generated in ADP with an average grain size of 75 μ. The results obtained were the averages of ten measurements. The relative experimental error was ±20%.

It follows from Eqs. (1) and (2) that, in contrast to single crystals, the second-harmonic flux in the case of powders is governed by all the nonlinear coefficients, by all the possible values of Δn, and the grain sizes; therefore, it is necessary to establish experimentally the presence of phase matching in order to estimate the efficiency of the nonlinear transformation of light.

In the presence of phase matching, some of the grains should be oriented along the phase-matching direction. Knowing the probability of grain orientation along the phase-matching direction and the grain dimensions, we can estimate the number of grains oriented along this direction. For example, in the case of a fundamental-frequency beam of 3 cm^2 cross section transformed in ADP with an average grain size of 75 μ, there should be $\sim 10^2$ such grains out of a total number of $\sim 10^4$. These grains generate the second harmonic proportionally to the square of the total grain size and therefore the contribution of the grains oriented along the phase-matching direction may be comparable with the output power of other grains and this contribution should increase as the grain size grows, if the number of grains is constant. However, when the grain size is increased, the number of grains decreases and this slows down the rise of the power of the second harmonic.

Figure 3 shows the experimental dependences of the power of the second harmonic component on the average grain size. It is evident from Fig. 3 that, in crystals of the phosphate group and in potassium tartrate, the second-harmonic power output increases with the grain size, whereas in the case of potassium–lithium sulfate and quartz (which do not have a phase-matching direction) the power is constant.

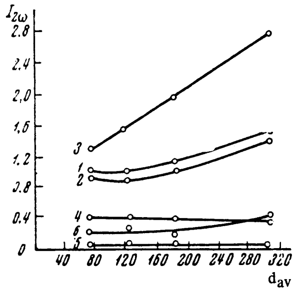

FIG. 3

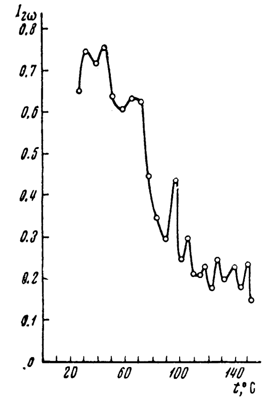

FIG. 4

FIG. 3. Dependence of the second-harmonic power on the average grain size in a sample (in microns): 1) ADP; 2) KDP; 3) RDP; 4) potassium-lithium sulfate; 5) quartz; 6) potassium tartrate.

FIG. 4. Temperature dependence of the second-harmonic power generated in RDA powder.

The influence of phase matching can be seen by considering, for example, RDA crystals. In these crystals, the phase-matching direction at room temperature makes an angle of ~80° with the optic axis. When the temperature is increased, the angle increases (because of a change in the refractive-index surfaces) and becomes 90° at t = 92°C,[8] when the phase-matching conditions break down.

Figure 4 shows the experimentally determined temperature dependence of the power of the second harmonic for an average grain size of 800 μ; the samples investigated were used without an immersion liquid. It is evident from Fig. 4 that, in the temperature range 90–140°C, the power of the second harmonic and its rate of change are considerably lower than in the temperature range 40–90°C, when the phase-matching condition is still obeyed.

Table I shows the comparative data for the second-harmonic power generated in powders with an average grain size of 75 μ and in corresponding single crystals, measured along the phase-matching direction.

A calculation, based on Eq. (2), yields satisfactory agreement with the experimental data for ADP and quartz of the same (75 μ) grain size. The ordinary and extraordinary wave fluxes of the second harmonic are calculated separately, using Eq. (1), and their sum is found. The calculated ratio of the second-harmonic flux generated in ADP to that generated in quartz is 26

Substance	Relative second-harmonic power		Substance	Relative second-harmonic power	
	powder	single crystals		powder	single crystals
ADP	1.0	1.0	DKDP	0.6	0.75
KDP	0.92	0.83	SiO_2	0.05	—
RDP	1.25	2.0	NaCl	0	—

and the experimental value is 20. This method was used[9] to confirm experimentally the possibility of detecting the existence of phase matching in powders of the substances investigated.

In a recent paper, Kurtz and Perry[10] reported that, in the case of substances exhibiting phase matching, the power of the second harmonic increased with increasing grain size up to ≈100 μ and this was followed by saturation, in contrast to the results shown in Fig. 3, where a linear rise of the power is still observed in the 75–300 μ range. This is evidently due to the fact that Kurtz and Perry[10] used constant-volume cuvettes in which the total number of grains decreased with increasing grain size $\bar{l}$,[1)] and consequently the number of grains oriented along the phase-matching direction decreased as $\sim 1/\bar{l}^3$, while we used a monolayer and therefore the number of grains decreased as $\sim 1/\bar{l}^2$. The use of a monolayer made it possible to eliminate the problems associated with a longitudinal distribution of the grains, such as the phase correlation, scattering, etc.

The ratio of the second-harmonic powers generated in ADP and quartz of ≈75 μ grain size was reported in [10] to be 15, which is in agreement with the results given in Table I.

In conclusion, the authors thank A. S. Sonin for discussing the results and T. P. Kalitina for her help in the experiments.

[1)] According to Kurtz and Perry [10], the power of the second harmonic increases proportionally to the total number of grains for grain sizes > 10 μ.

[1] R. W. Minck, R. W. Terhune, and C. C. Wang, Appl. Optics **5**, 1595 (1966).

[2] I. S. Rez, Usp. Fiz. Nauk **93**, 633 (1967) [Sov. Phys.-Usp. **10**, 759 (1968)].

[3] V. I. Bespalov, Izv. Vuzov, Radiofizika **9**, 1117 (1966).

[4] R. Yu. Orlov, Diploma Thesis, Moscow State Univ., 1964.

[5] K. E. Rieckhoff and W. L. Peticolas, Science **147**, 610 (1965).

[6] S. A. Akhmanov and R. V. Khoklov, Problemy nelineǐnoi optiki (Problems in Nonlinear Optics), VINITI, M., 1964.

[7] D. A. Kleinman, Phys. Rev. **128**, 1761 (1962).

[8] V. S. Suvorov and A. A. Filimonov, Fiz. Tverd. Tela **9**, 2131 (1967) [Sov. Phys.-Solid State **9**, 1674 (1968)].

[9] A. Graja, Phys. Status Solidi **27**, K93 (1968).

[10] S. K. Kurtz and T. T. Perry, J. Appl. Phys. **39**, 3798 (1968).

Translated by A. Tybulewicz
173