Analysis of nonlinear optical materials properties by simple powder technique

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Abstract. The article describes a simple technique for comparative analysis of the second harmonic generation properties of new samples and etalon materials by their powders. The effectiveness of the method was tested and measuring of nonlinear coefficient and damage threshold of the well known materials: KDP, LiIO3, m-nitroaniline was demonstrated. The parameters of the new promising nonlinear material DNPAP were measured.

1. Introduction
The first experiments for obtaining the second harmonic generation (SHG) of laser oscillation has been successfully implemented by Franken et al. on crystalline quartz [1]. These experiments were carried out in the same year, when the first laser was created. Thus researchers have found a simple way to get new laser frequencies. At present about fifty crystals have possibility of laser radiation frequency doubling but only few crystals are used in the lab. It is because a number of additional demands on the properties of crystals are associated with using their in practice. These properties are transparency region, processability of large-sized crystal growing, cost and etc. A number of chemical and physical properties such as hygroscopicity, optical homogeneity, radiation resistance, hardness, and thermal characteristics are further narrowing the list of the crystals. Therefore, a new nonlinear materials searching still is a very urgent task.

At the initial stage search for new crystals was very difficult. It is because it takes a lot of time to grow good optical quality new promising crystals of sufficient size for studies. This is required the development of crystal growth technology, which in turn requires a great financial and time resources. Nonlinear properties of these materials can be predicted using available modern theories. Their results are often confirmed by experimental measurements, despite their lack of accounting in the theory of other properties of studying materials, which influence on their nonlinearity. However, the actual values of nonlinear coefficients of new crystals ultimately are determined experimentally. But for these measurements single crystals samples require sufficient size. To solve this problem it is necessary to improve growth technology of these crystals, which is quite difficult and costly. It will be turned out especially more costly when the new crystal, for which growth technology was developed, after examining its nonlinear properties would be not promising. Therefore, along with the new SHG crystals creation the experimental techniques have been developed and are being developed. Some techniques allow measuring the nonlinear parameters of materials with minimal time and resources without using for these single-crystal samples. The development of such techniques is necessary for modern quantum electronics.

One of the ways that meet these requirements is the method of the nonlinear properties materials study proposed by S.K. Kurtz and T.T. Perry [2]. They first proposed systematic experimental study of...
nonlinear materials characteristics by powder method. This method has been widely used by experimentalists for a long time up to now. In this paper authors described the methodology of research with a well-developed at that time experimental setup. Method for sample preparation and technology of measurement was also described in detail. The experimental setup consisted of Q-switched laser and a photomultiplier with oscilloscope that determined the sufficient sensitivity for detecting radiation of SHG excited in the powders. The properties of a large number of new nonlinear materials, which presented in the paper, were measured in comparison with the intensity of the quartz SHG. In a later paper [3] Kurtz et al adduce a design description of analyzer, which is made in form of device, and its opportunity of studies of SHG and non-central symmetry powder materials properties. This device is based on experimental setup described in [2]. Created analyzer can detect materials SHG at the level of 1/1000 with respect to the quartz SHG. Paper [4] describes a method for the study of SHG in powders using inexpensive equipment. YAG:Nd$^{3+}$ laser operating in free-running mode was used to excite the SHG, which was cheaper, compared with Q-switched lasers for that time. It is well known that the pulse of free-running YAG:Nd$^{3+}$ laser is a train of microsecond pulses with a total duration equal to duration of the glow pumping lamp. Peak power of every microsecond pulse was enough for SHG and its registration by PMT. Signal was split and came to the photomultipliers, one of which was placed in the pump channel - the other one in the SHG test channel. Author applied integrator for registration of this signal. Concluding about SHG efficiency can be done from the ratio of PMT signals. In papers [5-6] authors suggested another powder method for studying properties of materials including the SHG parameters. Experimental setup scheme has the same dual-channel scheme with the PMT in each channel. Measure of the SHG efficiency of new materials by powder technique carried out as well with respect to quartz crystal SHG, which sample was installed in one of the channels. Feature of their setup was using of crystalline semi-spherical rutile (TiO$_2$) prism in the test channel. Powder of studied material was pressed by base of this prism. The powder sample was excited by evanescent wave (EW). It was partially emerged from the prism under total internal reflection from the surface to which the analyzed powder was pressed. As a result, authors solved the problem of the penetration depth of the radiation in the powder. Also with help of this prism by polarization way the SHG radiation was separated out from the main radiation. In paper [7] the idea of using EW in powder technique for test SHG properties of new materials got development in both directions as theoretical as experimental way. As a result they have shown the efficiency of using EW method for study properties of new materials in powder state. In their setup, powder was held tightly against the semi-cylindrical prism, which was placed on a double goniometer with angular movement controlled by computer. By this method, they studied and explored a number of new organic materials. It should be noted that the values of the effective nonlinear coefficient and refractive indices of the sample are obtained as fitting parameters of measured dependences. According to the authors, SHG signal from the EW is less sensitive to the phase-matching conditions for the material.

Thus, the powder method allows us to investigate the SHG efficiency of completely new synthesized crystalline materials for which single crystals growth technology is not known yet. First of all this method is necessary for chemists to intensify search for new effective nonlinear materials. But they continue to apply the setups built under the scheme of Kurtz and Perry that was designed in 1968. In this paper we describe a simple way, which is based on Kurtz and Perry method, for measuring parameters of new nonlinear materials by powder technique with using available modern equipment.

2. Basis of proposed powder technique

SHG coefficient determination by powder technique in the proposed method is based on a method of S.K. Kurtz and T.T. Perry [2] as mentioned above. In this method the SHG parameters of an unknown powder are compared with SHG of quartz powder. These parameters of nonlinearity for quartz were well known and also they previously have been determined for a single crystal.

In [2] the formula relating the intensity of the second harmonic $I_{2\omega, total}$ to intensity of the incident fundamental harmonic of the laser radiation $I_{\omega, ext}$ and the substance nonlinear optical coefficient $d_{2\omega}$ is
presented. It is important to take into account that the grain size of powder of the substance - \(r\) is much more than coherence length \(I_c = \frac{\lambda}{4(n_{2\omega} - n_\omega)}\).

Let’s consider the equation of the second harmonic intensity from the intensity of incident fundamental radiation.

\[
I_{2\omega}^{\text{total}} = \frac{32\pi}{c} (d^{2\omega})^2 \left[ \frac{64\pi I_{\text{ext}}^{\omega}}{2(n_\omega + 1)^2(n_{2\omega} + 1)} \right]^2 L \frac{l^2}{r} \sin^2 \left( \frac{\pi r}{2l_c} \right),
\]

where \(L\) is a thickness of plane-parallel slab, \(\lambda\) is a wavelength of fundamental optical signal. We divide it by the square of the fundamental radiation intensity:

\[
\frac{I_{2\omega}^{\text{total}}}{I_{\text{ext}}^{\omega}} = \frac{32\pi}{c} (d^{2\omega})^2 \left[ \frac{64\pi}{2(n_\omega + 1)^2(n_{2\omega} + 1)} \right]^2 L \frac{l^2}{r} \sin^2 \left( \frac{\pi r}{2l_c} \right).
\]

This ratio denote by the coefficient \(k\).

\[
k \approx \frac{I_{2\omega}^{\text{total}}}{I_{\text{ext}}^{\omega}} = k
\]

Then, we take the coefficients ratio of the sample and the standard.

\[
k_{\text{sample}} \approx \frac{d_{\text{sample}}^{2\omega}}{d_{\text{standard}}^{2\omega}} \left( \frac{n_{\omega \text{sample}} + 1}{n_{\omega \text{standard}} + 1} \right)^2 \left( \frac{n_{2\omega \text{sample}} + 1}{n_{2\omega \text{standard}} + 1} \right)^2 \frac{k_{\text{sample}}}{k_{\text{standard}}} \frac{l_{\text{sample}}}{l_{\text{standard}}} \sin^2 \left( \frac{\pi r}{2l_c \text{sample}} \right) \frac{\sin^2 \left( \frac{\pi r}{2l_c \text{standard}} \right)}{\sin^2 \left( \frac{\pi r}{2l_c \text{standard}} \right)}.
\]

It is evident that if the samples are equally prepared for determining this value we must know the corresponding coefficient for the standard, intensities of the incident and doubled frequency light and the refractive index of materials at corresponding wavelengths.

In practice, measurement of the nonlinear coefficient of new material in powder form reduces to the preparing powders with the same grain size as for powder of comparison crystal. Also the comparison crystals must have well known values of the nonlinear coefficients, for example KDP and LiIO\(_3\). For each powder sample measurement of SHG intensity dependences from the energy density of the incident laser radiation is need to register as much as possible in the identical conditions. Such dependencies have the form of the parabolas: \(E_{\text{shg}} = a + bx^2\), where \(b\) contains the nonlinear coefficient peculiar for the crystal powder for which this relationship is built. If we take into account the refractive indices for the incident and SHG waves in comparable materials, it is easy to directly obtain the ratio of their conversion factors from the ratio of the coefficients \(b\). In presence of the tabulated value of the corresponding coefficient for one of them - a reference sample, the required coefficient for another sample is easily calculated.

3. Samples

For demonstrating the performance of the proposed method we took the powders of KDP, LiIO\(_3\) and m-nitroaniline crystals with known values of nonlinearity from the literature. As an additional sample we took powder of a new synthesized material on which effect of SHG was visually observed, but the value of nonlinear coefficients was not known yet. This material was synthesized at the Institute of Chemistry, Kazan Federal University of Yu.G. Shtyrlin’s group. Abbreviation of this material is DNPAP [8].

Powders of the materials were prepared by mechanical milling of the crystals and sifting through calibrated sieves. For the experiments we took each powder sample of the crystals with the same grain size from 90 to 120 \(\mu\)m.

4. Technique of experiment

For determination of nonlinear coefficients of new materials in powder form, which are due to SHG, we used experimental setup, which concept is displayed in figure 1.
The scheme of the experimental setup for determining nonlinear coefficients of materials in powder form by SHG: 1 - YAG:Nd\(^{3+}\) laser, 2 – 90-degree prism, 3 - focusing lens, 4 - sample of powder on the substrate, 5 - a table with fiber mount, 6 - quartz optical fiber, 7 - «StellarNet» spectrometer.

Radiation of the fundamental harmonic of YAG:Nd\(^{3+}\) laser (1), was turned via prism (3) so the beam fell on a sample vertically. Then, the radiation focused by the lens (2) on the sample of the investigated powder (4). Sample of the powder prepared in a special way on a special substrate (see details below). It was placed on a special table (5) with a fiber which was attached to it (6). The other end of the fiber was connected to the spectrometer StellarNet (7), which was used for recording the emission spectrum of SHG of the powder.

For the most accurate determination of the b coefficients of comparable materials in powder form it was needed to perform two conditions. Firstly, it was needed an equal preparation and identical installation of each powder sample on the table of experimental setup. Secondly, for the r>>lc condition implementation it was needed to choose the identical spot diameter of pumping radiation for both samples taking into account the particle size of this powder materials. To perform first condition mentioned above we used substrate with a special groove. This groove had depth satisfying the condition h>>l for laser penetration depth (3-4 mm more than enough). The sample of powder freely without compaction was poured into the groove. Its excess was equalized by smooth straight edge of a plate against edge of the groove. After that, the substrate was mounted on a horizontal table (5) with special detents for its uniform installation. Thus, the experimental conditions to excite the SHG for each powder sample were reproduced identically as closely as possible. Diameter of the spot of the incident radiation was not less than 1 mm, that at a particle size of 100 \(\mu\)m is fully satisfy to the second condition.

Incident and converted radiation in the form of two spectral lines were recorded on spectrometer (7). This spectrum included the following components: specular and diffuse scattering of fundamental harmonic of the laser and the conversion signal due to the SHG of researched substances. Operational control of radiation intensity changes of the fundamental wave and of second harmonic by maxima on the spectrum was carried out. Additionally the energy of the laser fundamental harmonic was controlled by “Ophir” power meter. Its measuring head (on the figure is not shown) was set in place of a table (5) and during main experiment it was removed.

Also, in our experiments we performed measurements of damage threshold of researched samples under the influence of multiple laser pulses. For this, the samples were exposed to several tens of thousands pulses of fundamental harmonic of YAG:Nd\(^{3+}\) laser. The damage threshold of the samples was controlled by several methods. Firstly, it has determined by dislocation of quadratic dependence of the SHG intensity on the density of the incident radiation. Secondly, it was defined with a constant energy density of the laser pulses by decreasing of SHG intensity on the number of laser pulses. Thirdly, the ultimate control of samples destruction presence was performed by analysis of them under a microscope. Thus we obtained sufficiently reliable data on the damage thresholds of the studied samples.
5. Results and analysis of them

During the work the measurements were made and relationships of changes in the SGH intensity for all four samples – LiIO₃, KDP, m-nitroaniline, and DNPAP from the energy density of the laser incident radiation were described. The results of measurement were plotted as graphs which are shown in figure 2.

![Graph of SHG intensity vs energy density](image1)

**Figure 2.** SHG intensity of samples (1 - LiIO₃; 2 - KDP; 3 - m-nitroaniline; 4 - DNPAP) versus incident radiation energy density of a pulsed YAG:Nd³⁺ laser.

The obtained dependences are well approximated by a quadratic function, as it is shown for LiIO₃ sample in figure 3.

![Graph of SHG beam intensity vs energy of laser](image2)

**Figure 3.** SHG beam intensity dependence data for LiIO₃ sample vs the incident radiation energy density of a pulsed YAG:Nd³⁺ laser, which was approximated by quadratic function.

This is due to the fact that the dependence of frequency conversion has a view of quadratic function as a rule. The resulting parameters of approximation of experimental data are the parameters of
frequency conversion of studied samples. Namely, the coefficient of the quadratic part data is due to the nonlinear coefficient of sample. This approximation has been made for each graph data, which is shown in figure 2, and thus b coefficients were determined for each sample. From the ratio of the b coefficients for samples with unknown nonlinear coefficient to the b coefficient for sample with known one, in accordance with their refractive index data, the values of nonlinear coefficient $d^{2\omega}$ were calculated for each sample. The corresponding results are shown in table 1.

Table 1. The data of laser-optical properties of the studied crystalline materials.

| Crystal      | Normalized nonlinear coefficient | Absolute nonlinear coefficient (m/V) | Damage thresholds (multiple pulses) (W/cm²) |
|--------------|----------------------------------|--------------------------------------|---------------------------------------------|
| KDP          | 1                                | $6.3\cdot10^{-13}$                   | $1\cdot10^{10}$                            |
| LiIO₃        | 11.16                            | $7.03\cdot10^{-12}$                  | $2.1\cdot10^{10}$                          |
| m-nitroaniline | 9.08                            | $5.72\cdot10^{-12}$                  | $2.3\cdot10^{10}$                          |
| DNPAP        | 6.44                             | $4.06\cdot10^{-12}$                  | $4.4\cdot10^{10}$                          |

* The data were taken from literature [9]

Thus in the table 1 we gave data of the nonlinear coefficient for each studied sample normalized with respect to KDP; the absolute nonlinear coefficient values calculated from the relative coefficients, with using data known from the literature for the KDP; the damage thresholds against multiple laser pulses.

The obtained results were compared with reference data for the widely known crystals described in the literature [9]. In this article value of $d^{2\omega}$ coefficient at a wavelength of 1.06 μm is equal $7.02\cdot10^{-12}$ m/V for LiIO₃ crystal. As we can see, the data from this article is in a very good agreement with data from table 1. The optical damage thresholds data of the studied materials have a good agreement also [9]. This proves the correctness of the methodic, which is described in this paper.

So, the date that we received for the new material DNPAP is also correct. The above data allow us to tell about the promising of DNPAP material as an SHG material. It is due to the rather large value of the nonlinear optical coefficient comparable to LiIO₃. Also, as we can see from table, this new material has large optical damage threshold – about two time more than for materials, which taken for comparison in the work.

Thus, by the work it was demonstrated simple and effective method of measurement of nonlinear properties of a new material.

6. Conclusion
Simple technique for analyzing of new nonlinear optical materials properties has been developed and demonstrated on well-known crystalline materials. Nonlinear coefficient and damage threshold of KDP, LiIO₃, m-nitroaniline of the samples were measured. The data coincided with data known from literature.

Nonlinear-optical parameters for new promising nonlinear material - DNPAP were measured. The values of these parameters allow us to hope to apply of this material in practice.

Acknowledgments
This work supported by RFBR, research project No. 14-02-31299 mol_a.

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