SHG in γ-Ga_2S_3 powder

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ABSTRACT

We report results on comparative study of SHG in powder of promising nonlinear γ-Ga_2S_3 crystal. Digallium trisulfide powders with particle size from 20 μm to 500 μm were tested in comparison with powders of well-known LBO, BBO, KABO, KDP, and LN nonlinear optical crystals under the pumping by a 7 ns 1064 Nd:YAG laser. Laser-induced damage threshold of different powder fractions were determined. Powder of γ-Ga_2S_3 shown high damage threshold and large SHG intensity: 56 times to that in LBO powder, 15 in BBO, 50 in KABO, 67 in KDP, and 3 in LN (for particle size: 20–50 μm), that renders it amongst the most promising crystal for frequency conversion of high-intense nanosecond radiation of near-IR lasers by optical rectification technique.

Keywords: Digallium trisulfide, nonlinear crystals, second harmonic generation, Kurtz–Perry powder technique, laser-induced damage

1. INTRODUCTION

The search for novel nonlinear optical (NLO) crystals for parametric frequency conversion is still relevant task due to necessity of improving the efficiency of the laser systems both operating from the visible to the mid-IR range, and in the THz range. Obtaining bulk optical single-crystals requires a great deal of time and resources. Therefore, in order to reduce costs it is interesting to determine nonlinear optical properties using more accessible and cheap powder materials. For example, the Kurtz–Perry method developed in the late 1960s makes it possible to estimate nonlinear coefficients in powders and determine whether the phase-matching condition is achievable or not [1]. This approach is particularly valuable at the stage of development of growth technology, when it is not possible to create a single-crystal sample of sufficient size. A detailed discussion of the possibilities of this method is presented in [2-4].

Digallium trisulfide one of the potentially promising nonlinear optical crystal [5, 6], which is transparent in wide spectral range, including the THz domain [7]. This crystal exists in several polytype modifications [6], all of which may be of interest for nonlinear optical application. Previously, we had already investigated the properties of cubic γ-Ga_2S_3 modification (from here and next γ-Ga_2S_3), which was obtained from $PbCl_2$ solution [6]. However, the intercalation of $PbCl_2$ into the Ga_2S_3 lattice led to the transformation of crystal structure and substantial deterioration of its optical properties, including a decreasing of the Nd:YAG laser second harmonic generation efficiency.

In this work, a comparative analysis of SHG of the nanosecond pulses of Nd:YAG laser in γ-Ga_2S_3 powder versus SHG in powders of well-known LBO (LiB_3O_5), BBO (β-BaB_2O_4), KABO ($K_2Al_2B_2O_7$), KDP (KH_4PO_4), and LN ($LiNbO_3$) nonlinear crystals under identical experimental conditions was made by the Kurtz–Perry method.

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2. MATERIALS

Powder of γ-Ga_2S_3 was obtained by the solution method given in [6], with substitution of $PbCl_2$ solvent by KI. After synthesis, the material from the growth ampoule was washed up in dimethylformamide, which dissolved KI and did not affect Ga_2S_3. The result material was a pale yellow powder with grains up to several millimeters size. The crystal structure of the obtained samples was established by XRD method using a XRD-6000 (Shimadzu, Japan). The investigated samples, as expected (since they were synthesized under conditions analogous to [6]), had a cubic structure, F-43m crystallographic space group.

A typical SEM image of the synthesized crystals surface, obtained with a scanning electron microscope VEGA 3 SBH (Tescan, Czech Republic), is shown in Figure 1; macro defects, precipitates and caverns are clearly visible.

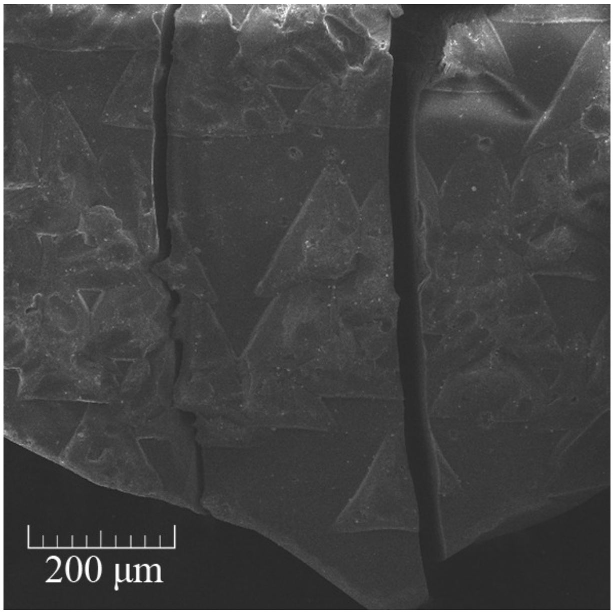


Figure 1. SEM pictures of bulk defects on the surface of γ-Ga_2S_3 crystals.

A number of well-known commercial NLO crystals with different structure and nonlinear susceptibility were chosen as reference samples. Information on the NLO properties of commercial samples used in the comparative study is provided in Table 1.

Table 1. Reference data on NLO properties of selected crystals.

Name	BBO [8-10]	LBO [8-10]	KABO [8-10]	KDP [8, 10]	LN [8, 10]	γ-Ga_2S_3 [5]
Crystal class, HM	Trigonal, 3m	Orthorhombic, mm2	Trigonal, 32	Tetragonal, -42m	Trigonal, 3m	Tetrahedral, -43m
Type	Negative uniaxial	Biaxial	Negative uniaxial	Negative uniaxial	Negative uniaxial	Isotropic
n_o/n_e (at 532 nm)	1.67/1.55	1.58/1.61/1.62	1.56/1.49	1.51/1.47	2.32/2.23	n ~ 2.6
$\lvert d_{ij}\rvert$ (pm/V) (at 1064 nm)	$d_{15} = 0.03$ $d_{22} = 2.2$ $d_{33} = 0.04$	$d_{31} = 0.67$ $d_{32} = 0.85$ $d_{33} = 0.04$	$d_{11} = 0.46$	$d_{36} = 0.39$	$d_{22} = 2.1$ $d_{31} = 4.35$ $d_{33} = 27.2$	$d_{14} \sim 24$
Transparency window (μm)	0.19–3.5	0.15–3.2	0.18–3.6	0.18–1.4	0.4–5.5	0.6–20 [6]

3. EXPERIMENTAL

3.1 Sample preparation

Selected crystals were crushed and fractionated using a set of sieves with a calibrated mesh size of 20–50 μm, 50–100 μm, 100–160 μm, 160–250 μm and 250–500 μm. Size of the obtained particles was checked by means of an optical microscope. The presence of macro defects did not affect the quality of the prepared powder because of the shallow structure of the latter. To confirm the absence of absorption in the pump and second harmonic wavelengths (1064 nm and 532 nm, respectively), diffuse reflectance spectra for the smallest fraction of the powders were recorded. A Cary 100 spectrophotometer (Varian, Australia) was used in the wavelength range 350–900 nm and a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, USA) was used in the range of 900–5000 nm. From the spectra obtained, γ-Ga_2S_3 edge of the absorption band was determined, which turned out to be identical with that given in [6].

3.2 Second-harmonic generation by Kurtz–Perry powder technique

Kurtz–Perry method allows one to evaluate values of the effective nonlinear optical coefficient, which may be written in the general form [11]:

$$d_{eff} = \sum_{ijk} d_{ijk}(-\omega_3, \omega_1, \omega_2)\cos(\alpha_i^{\omega_3})\cos(\alpha_j^{\omega_1})\cos(\alpha_k^{\omega_2})\,, \tag{1}$$

where: d_{ijk} – nonlinear coefficients, a_i, $i = 1...3$, angles between the plane of electromagnetic waves and the optical axes of the crystal. SHG intensity can be defined as [12]:

$$I(2\omega) \propto \frac{d_{eff}^2}{n^2(\omega)n(2\omega)} L^2 I^2(\omega)\,. \tag{2}$$

It follows from the expression (2) that for a fixed thickness L of the sample, the SH intensity should increase quadratically with pump intensity. The magnitude of the SH signal obtained from powder under test can be compared with SH signal from powder with known NLO parameters. Consequently the nonlinear figure of merit ($d^2 \cdot n^{-3}$) for tested powder can be found.

To study the efficiency of SHG in powder samples of NLO crystals, a modified Kurtz–Perry scheme was prepared (Figure 2).

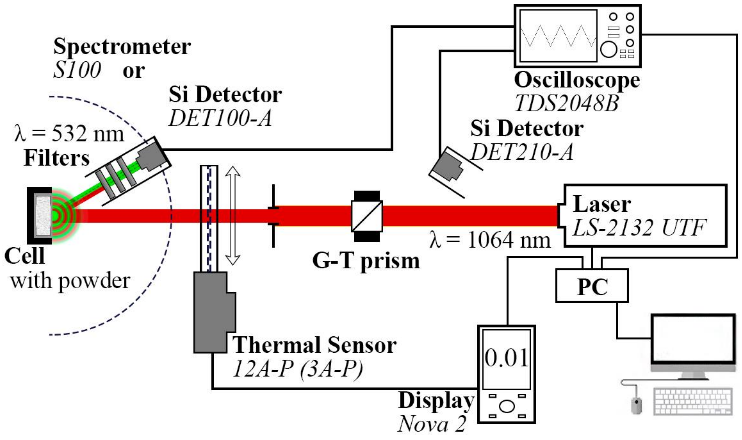


Figure 2. Principle scheme of second-harmonic generation powder test.

The unfocused radiation of a Nd:YAG LS-2132UTF laser (LOTIS TII, Belarus) with a wavelength of 1064 nm and approximately 7 ns pulse duration is guided through a Glan-Thompson prism (allows to control density of the incident radiation power in the 2–80 MW/cm^2 range) on the cell with powder under test. Diffusive reflected laser radiation and second harmonic radiation pass through the set of light filters BGG 23-26 (Standa, Lithuania). Filters are opaque at

1064 nm, but transparent at 532 nm; only second harmonic radiation can pass through them. Filters and a photodiode DET100A (Thorlabs, Germany) are isolated with an opaque screen to prevent the entry of background light. A DET210 (Thorlabs, Germany) photodiode starts an oscilloscope TDS 2024b (Tektronix, USA) scan. The laser intensity is determined with a 12A-P thermal sensor (Ophir, Israel).

Figure 3 shows the obtained dependencies of the SHG intensity from the laser pump intensity for one of the powder fractions.

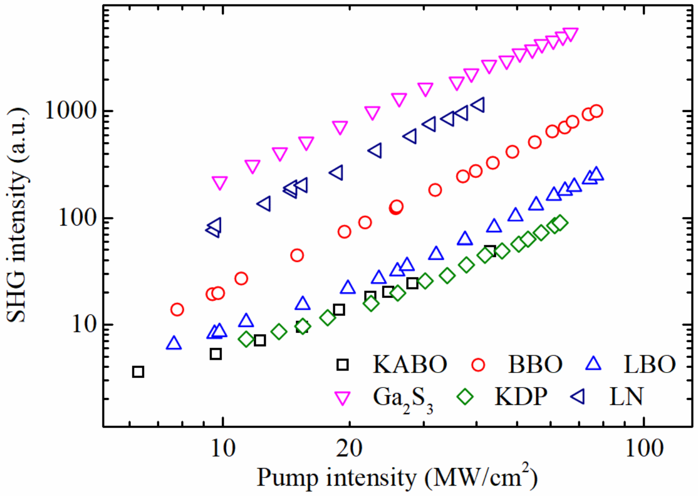


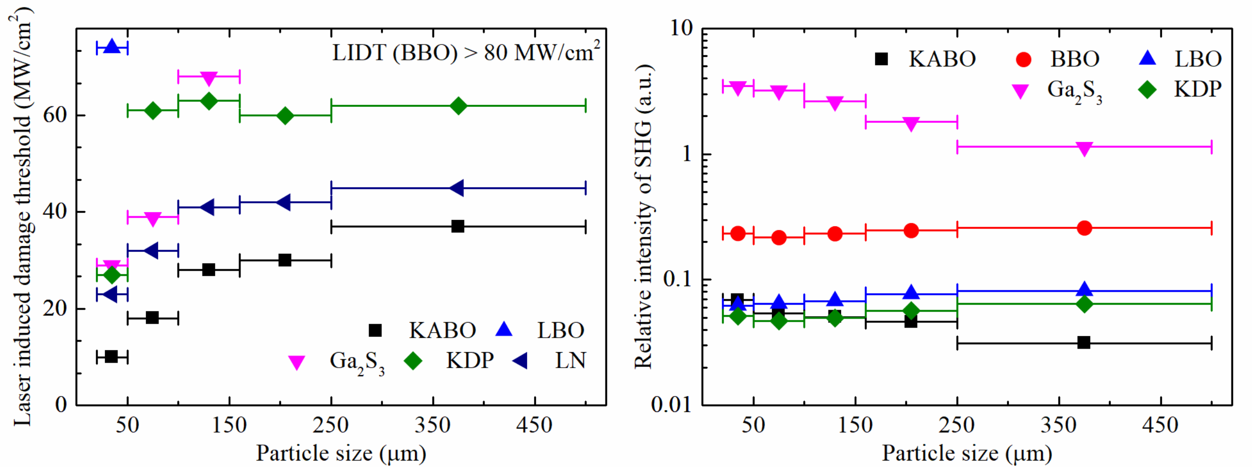
Figure 3. Typical SHG intensity of 100–160 μm powders.

It was established that powders of different nonlinear crystals had different thresholds of laser-induced breakdown. Thus, if BBO and LBO powders efficiently generate at a pump power density of the incident radiation ~ 80 MW/cm^2, a LN powder could be already damaged at 40 MW/cm^2. To compare the SHG intensity, such pump intensity, at which the laser-induced destruction of the powders is still not observing, was chosen. At a given pump intensity, for phase matchable crystal powders SHG intensity is increasing with the increasing the particle size unlike the decreasing in non-phase-matchable crystal powders [1, 3].

4. RESULTS AND DISCUSSION

Dependencies of laser induced damage threshold and relative SHG intensity on the average particle size for each powder fraction are shown in Figure 4a, b.

Figure 4 shows that significant permanent change of characteristics does not occur in 100–150 μm powders of LBO, BBO and Ga_2S_3 nonlinear crystals up to pump intensity of 80 MW/cm^2, 70 MW/cm^2 for Ga_2S_3, while the efficiency of SHG in LBO and BBO powders is at least 5 times less than that in Ga_2S_3 powder. For the remaining nonlinear crystals, laser-induced damage threshold is in the range from 25 MW/cm^2 to 65 MW/cm^2, for the powder of the most efficient LN nonlinear crystal it is only about 40 MW/cm^2. According to the obtained data, a pre-threshold pump intensity was established. For this pump intensity, SHG efficiency for all fractions of the investigated powders were determined. For each nonlinear crystals powder fraction, we obtained dependencies like those in figure 3. Experimental points of SHG intensity were approximated by a second-order polynomial according to (2). Using known d_{ij}, according to the formulas given in [3] for the powder of LN nonlinear crystal, effective nonlinear coefficient can be determine as: d^2_{eff} = 16.6 pm^2·V^{-2}. Then using the expression (2) with respect to the ratio of SHG intensity from γ-Ga_2S_3 and LN powders, d^2_{eff} for digallium trisulfide was estimated as 92.0 pm^2·V^{-2}.



a b

Figure 4. Dependences of laser induced damage threshold (a) and relative intensity of SHG on powder size (b) of NLO crystals.

It can be noted that SHG efficiency in KABO powder decreases with increasing of fraction size. According to [8], for a given nonlinear crystal at a wavelength of 1064 nm, phase-matching can be achieved. According to the theory of the Kurtz–Perry method, with the increase of the fraction size, the intensity of SHG should increase too. This effect can appear because the powder under investigation was obtained from a polycrystalline druse of KABO NLO crystal. For the powder obtained from such a material, increasing the fraction does not result in an increase of the single crystals size, and the effective path of SHG does not increase, respectively. This is unlike an increase in SHG intensity with increasing of particle size for LN, LBO, BBO, and KDO powders obtained from bulk single crystals. This effect could also affect efficiency of SHG in γ-Ga_2S_3 powder that was also obtained from a polycrystalline druse.

A bulk γ-Ga_2S_3 crystal is isotropic i.e. phase matching conditions cannot be achieved [4]. However, crystals of this point group have non-zero effective second-order nonlinear susceptibility coefficients [2]. They possess a moderate high value of the established nonlinear susceptibility coefficients and high laser-induced damage threshold. Thus, thin plates made of this crystal with a characteristic size not exceeding the coherence length can be used for efficient nonlinear optical rectification.

The SHG of γ-Ga_2S_3 powder obtained in [5] is equal to half of that in a $KTiOPO_4$ (KTP) powder. In this study, we found the SHG intensity in powder of γ-Ga_2S_3 is 3.5 times and 1.2 times greater than that in powder of LN nonlinear crystal for a particle size of 20-50 μm and 250-500 μm, respectively. Cubic and monoclinic phases of Ga_2S_3 has a transparency window in the range 0.44-25 μm [6] that exceeds transparency range 0.6–20 μm of the GaSe nonlinear crystal [8]. In [6, 7] it is also shown that phonon absorption bands are absent in Ga_2S_3 in a wide part of the THz range.

5. CONCLUSION

Tested powders of digallium trisulfide NLO crystal showed high efficiency of SHG and high laser-induced damage threshold under exposure to nanosecond Nd:YAG laser pulses. The intensity of SHG in a powder of γ-Ga_2S_3 nonlinear optical crystal for the fraction of 20–50 μm established to be ~ 3.5 times higher than that in LN powder and is 67 times higher than in KDP powder. The laser-induced damage threshold for γ-Ga_2S_3 appears to be much higher than that in KDP, LN, and KABO powders. These optical properties allow one to consider γ-Ga_2S_3 as a highly promising material for optical rectification in an extremely broad spectral range. It is also promising to produce periodic structures of this material for a quasi-phase-matched frequency conversion, and it would be of interest to perform a phase-matched frequency conversion at the wavelengths region of its anomalous dispersion.

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