Optical rectification and down-conversion of fs pulses into mid-IR and THz range in $GaSe_{1-x}S_x$

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ABSTRACT

Design of top S-doped GaSe growth technology is completed. New methods for characterization of high optical quality crystals are proposed that allowed selection optimally doped crystals. Frequency conversion of fs pulses into 6.5-35 μm and into 0.2-4.5 THz is realized. S-doped crystals demonstrated advantages from 50-70% in the first experiments up to 8.5-15 times in the following experiments depending on experimental conditions.

Keywords: nonlinear crystal, GaSe, $GaSe_{1-x}S_x$, fs pulse, optical rectification, down-conversion, mid-IR, THz

1. INTRODUCTION

The ε-polytype of gallium selenide (hereinafter GaSe) promises efficient parametric frequency conversion over a large range of wavelengths. The performance potential of GaSe, which belongs to point group symmetry $\bar{6}m2$, is due to its extreme physical properties. Its wideband transparency range between 0.62-20 μm continues at wavelengths ≥50 μm[1,2]. Other attractive physical properties are giant birefringence B=0.375 at λ=10.6 μm and 0.79 at THz range[3], very high second order nonlinear susceptibility d_{22}=54 pm/V at 10 μm[4] and 24.3 pm/V in the THz band[5]. GaSe is second-highest among mid-IR anisotropic nonlinear crystals for optical damage threshold[6, 7] and thermal conductivity in the plane of growth layers (0.162 W/cm·deg.) that is accompanied by large thermal capacity C_p=47.9 J/(mol·deg.) and density 5.05 g/cm^3, close coefficients of linear thermal expansions $\alpha_{\parallel}=10.8\cdot10^{-6}$/deg. and $\alpha_{\perp}=9.1\cdot10^{-6}$/deg., and low two-photon absorption coefficient 0.2-0.5 cm^{-1}/GW for 0.7-0.8 μm pump[8]. For the first time GaSe was used for laser frequency conversion within the mid-IR in 1972[8,9]. In subsequent years, it was widely used for in-door mid-IR applications[4]. Over the past two decades, it is among the most promising anisotropic crystals for efficient generation within extra broadband 0.8-5640 μm (with the exception of the phonon limited gap around 46 μm) using birefringent phase matching[8,10-13]. However, promising properties have not allowed it to achieve the ubiquity of other nonlinear crystals such as anisotropic $ZnGeP_2$ or isotropic ZnTe and LT-GaAs in practical applications. This is because GaSe is difficult to grow and process as large high optical quality (absorption coefficient α≤0.1-0.2 cm^{-1}) single crystal samples[14-16] due to its layered structure with weak inter-layer Wan-der-Waals type bonding[8]. Its hardness has been measured as close to "0" on the Mohs' scale[8]. Limited optical quality of grown GaSe crystals is caused by technologically weakly controlled defects: point defects (mainly Ga vacancies) and micro-defects (Ga precipitates, voids or bubbles, stacking disorders, broken layers and dislocations)[17-19]. As a result, physical properties of GaSe are strongly dependent on the state-of-the-art of the growth technology.

Fortunately, GaSe is a good matrix material for doping with various impurities. An original ε-polytype structure of GaSe is strengthened by doping; meanwhile, the physical properties, which are responsible for the efficiency of frequency conversion, may be noticeably modified**.** Most impressive results are achieved by S-doping that is leaded to 2-3 times decrease in the absorption coefficient, 4-5 times increased optical damage threshold at optimal S-content of 2-3 mass%, and over 50% larger hardness. Recently, improved physical properties of doped GaSe crystals were described in details in Ref. 7, 20-23.

By using doped crystals, attractive results were demonstrated on frequency conversion of long (nanosecond)[24-29] and ultrashort (ps and fs) pulses[27,30,31]. In this work we overview highlights some of the progress that has taken place in our development of frequency converters of near IR femtosecond lasers into mid-IR and THz range within last decade.

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2. GROWTH TECHNOLOGY

Pure and doped GaSe crystals are obtained by modified syntheses and vertical Bridgman growth method. In principle, the synthesis of GaSe during the growth process is possible. However, a high Se pressure at the melting point of 938°C[32] suggests to synthesize the polycrystalline compound by separate procedure. Two-zone syntheses method[33] was exploited in this study. In accordance with this method, Ga is placed in the "hot" zone of the ampoule, while the other part with Se is slowly heated in the "cold" zone according to the progress of synthesis reaction. We preferred to use single zone furnace with gradual moving of the ampoule inside[34]. This technique seems to be more reliable, because one may estimate the vapor pressure inside the ampoule visually by its color. To improve optical quality of the synthesized polycrystalline material synthesis is conducting by using quartz ampoules that are charging with a large amount, up to 65% in volume, to decrease rest gases quantity and in such a way to improve the material quality. Charge materials were preliminary carefully purified by multiple re-melting. Synthesized material is stored in sealed ampules before transferring into single or double wall ampoule for crystal growth. Growth ampoules covered with pyrolytic carbon are used to exclude interaction with the quartz wall to prevent deformation of grown boulles. Other details on the growth process can be find elsewhere[34,5]. Namely, S-doped or GaSe:S(0.05, 0.15, 0.3, 0.5, 0.9, 1, 2, 2.3 2.5, 3, 4, 5, 7, 10, 10.2, 11, 100 mass%) crystals that also referred to as crystals of solid solutions $GaSe_{1-x}S_x$, x=0.002, 0.007, 0.014, 0.023, 0.04, 0.046, 0.09, 0.103, 0.112, 0.133, 0.175, 0.216, 0.294, 0.406, 0.412, 0.44, 1) were grown and studied. External view on some of them is shown in Fig.1.

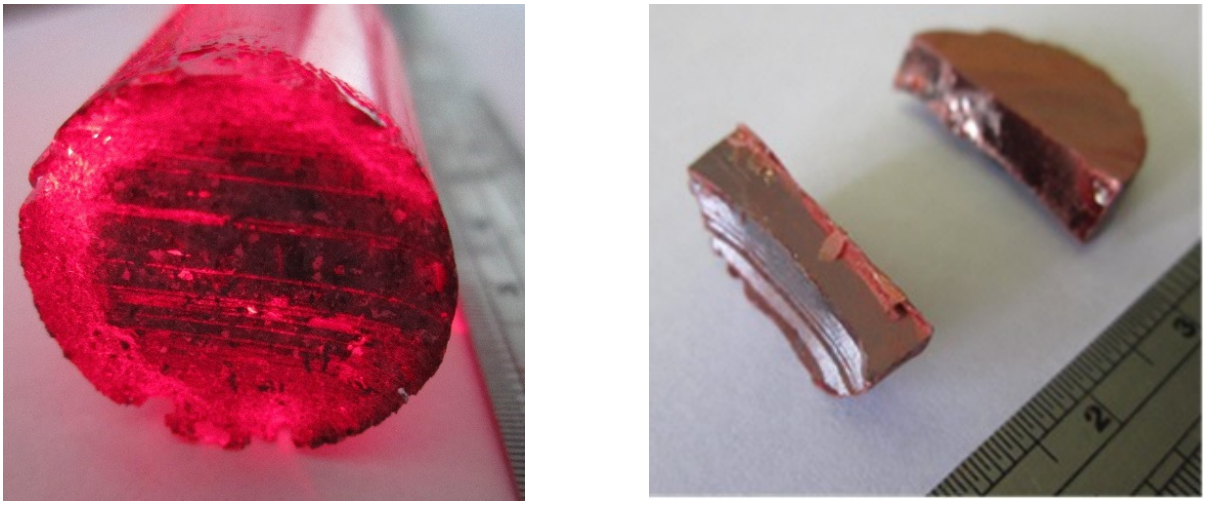

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Figure 1. (a) External view at cleaved GaSe single crystalline boule and (b) SEM image of side view of its layered structure (balls are precipitated Ga drops).

Visual inspection of as-grown crystals didn't show any color differences between initial and final sections of boules; its high optical quality can be estimated by naked eye, evident in its transparency and homogenity. In Fig. 1 it is seen that eutectic is negligible and layered GaSe structure can be seen through it. End section of the boule can be easy cleaved that confirm its top quality.

3. CRYSTAL CHARACTERIZATION

Modern facility of Tomsk State University, Tomsk, Russia, National Chiao Tung University, Hsinchu, Taiwan and Jilin University, Changchun, China was used to study physical properties of grown S-doped crystals[7,20,21,23].

Some difficulties were met in the crystal characterization. Due to limited penetration, polytype composition of GaSe cannot be established by X-ray methods, through-out bulk crystals. The polytype structure of the observed specimens in our study were identified, by a proposed non-linear method, through the comparison of the φ-angle dependence of frequency conversion efficiencies for different types of three wave interactions[36]. In Ref. 36 a nonlinear method for determining optical uniformity is also presented. We proposed selection criteria, determined by absorption measurement outside of the maximal transparency range, by examining the parameters of the exiton and phonon absorption peaks[37,38]: the larger the peak magnitude and the narrower the spectral bandwidth, the better the quality. Validity of this method is

confirmed by the efficiency of different frequency conversion processes. To select adequate data of THz-TDS measurements original criterion was proposed as quality of etalon patern[22].

It was established that S-doped GaSe crystals are still belonging to ε-polytype $\bar{6}2m$ point group structure similar to that for GaSe and possesses layer structure with ≥50% higher hardness and higher cleavage. Nevertheless, modified growth technology allowed us to control physical properties of GaSe by S-doping within broad limits. S-doping with 11 mass% shifts the short wave edge of GaSe transparency window down to 0.54 μm. In line, the long wave edge is shifting down to 14 μm. Absorption coefficient is decreasing for 2-3 times in both the mid-IR and the THz range in comparison to that for crystals grown by common Bridgman technology. Nonlinear absorption coefficient decreases for up to 7 times (here absolute values of the absorption coefficient magnitudes is still a subject for discussion). It was also found that e-wav absorption coefficient in the THz range is smaller than that for o-wave at least for 3 times that make preferable e-wave generation.

In fact, until current time, we paid main attention to improve crystal growth technology, crystal characterization, software design to estimate phase matching and potential efficiency, and application for long pulse frequency conversion. On the other hand, broad transparency range is resulting in small group velocity dispersion (Fig.2) for pure and doped GaSe.

PM diagrams are following shifted transparency range that allow optimization of frequency conversion efficiency for fixed wavelength pump by S-doping control (Fig.3).

In Fig.3 it is sen that PM angles can be controlled within at least 17° for near IR pump lasers that should be (and is resulting) in 20% increase in frequency conversion efficiency.

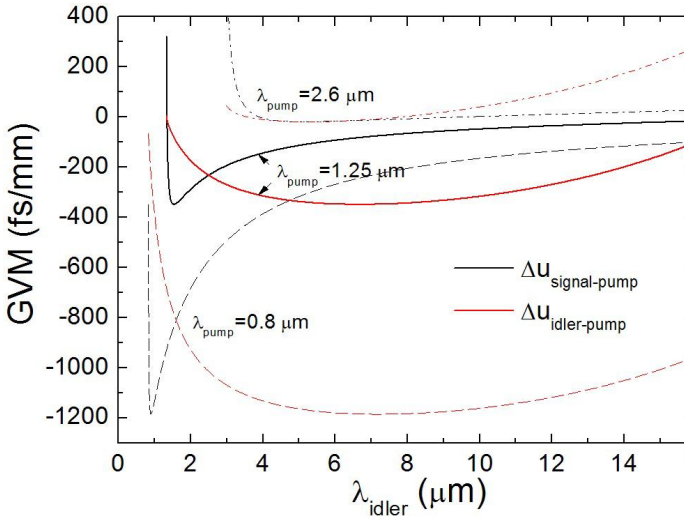

Figure 2. Group velocity mismatch for GaSe at pump wavelength as a parameter.

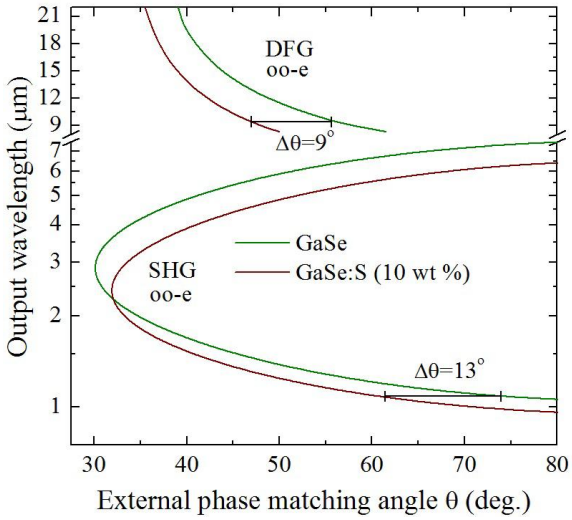

Figure 3. SHG and DFG phase matching of fs OPA (1.1-2.9 μm) pulses.

4. FREQUENCY CONVERSION OF FS PULSES

By using Ti:Sapphire laser emitting 30 fs pulses at 800 nm with spectral bandwidth 35 nm as a pump source and pure and S-doped GaSe crystals as frequency converters we generated mid-IR fs pulses frequency tunable within broad spectral range 6.5-24.5 μm (Fig. 4) at pulse repetition rate 80 MHz and few tens of pJ single pulse energy.

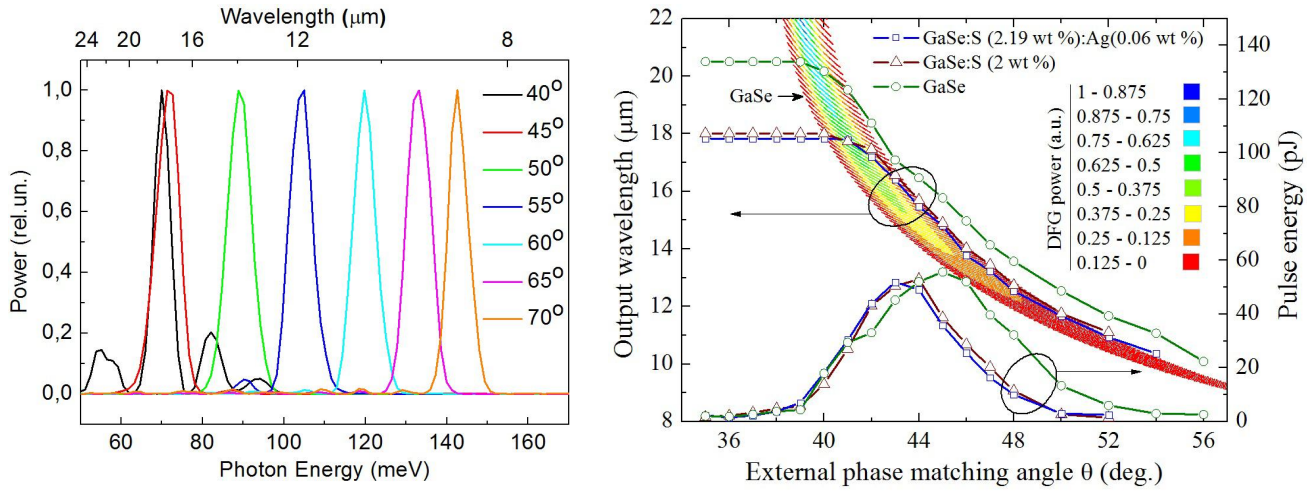

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Figure 4. An example of fs pulses generated by phase matched down-conversion of 30 fs Ti:Sapphire laser: (a) versus incident angle as a parameter, (b) upper limit of the output wavelength and energy of generated single pulses.

Common type optical set-up and homodyne MCT detector were used in this experiment. By using liquid-helium- cooled Si bolometer generation up to over 35 μm was detected. Generation range can be extended towards short wave simply by using shorter pulse pump fs laser. Generation efficiency was increased over than for about 20 times by mixing output emissions of two fs pump sources OPA TOPAS-C (Coherent). OPA TOPAS-C are tunable within 1.1 – 2.9 μm and generating 60-90 fs pulses in dependence on generation wavelength. Two 2-mm thick crystals were used under PM conditions. Generation spectrum is found too complicated (Fig.5).

It was found that so complicated output spectrum is due to multiprocess parametric frequency conversion: DFG, one stage OPG under the pump of each beam and two stage OPG under the pump by idler wave beam of the first stage. It was estimated occurs because giant birefringence and small group velocity mismatch for interacting and generated waves. Total conversion efficiency exceeded 50% in spite of the fact no selection of interaction type, optimization of crystal parameters or temperature, or maximization of the pump intensity were made.

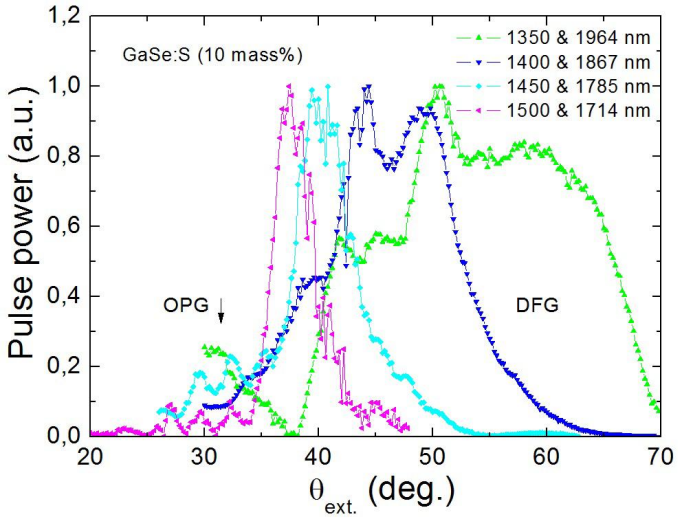

Figure 5. Power of the frequency converted emission on the output of monochromator under the pump by 4 identified pairs of pump beams at different wavelengths versus crystal orientation.

Optically rectified THz pulses generated in S-doped GaSe in the first experiments under the pump by 35 fs Ti:Sapphire laser pulses and detected by free space ZnTe detector are shown in Fig.6.

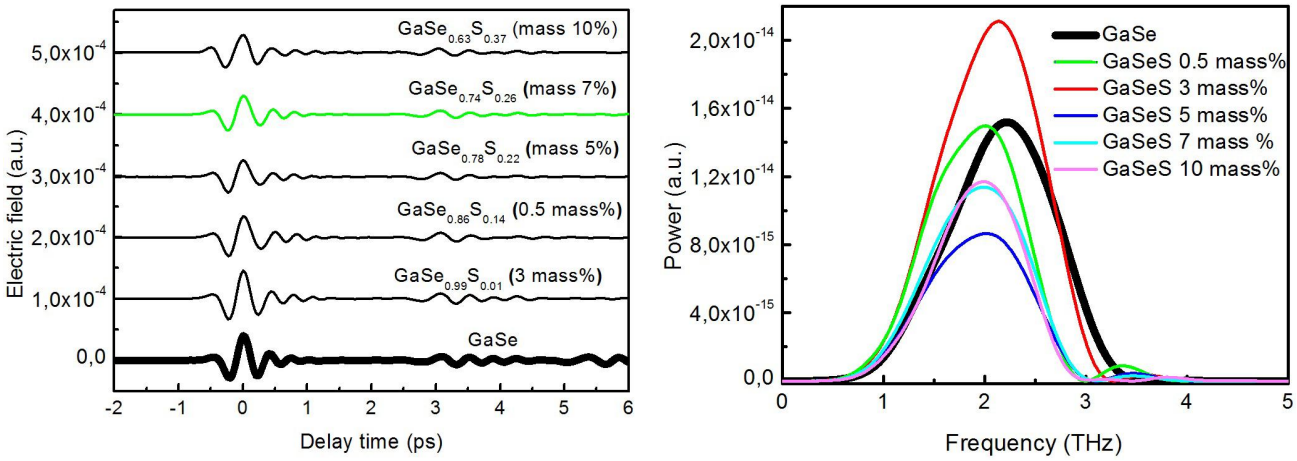

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Figure 6. (a) Electric field on the output of free space detector and (b) spectral composition of rectified (THz) pulses.

Later generation range was extended to 0.2-4.5 THz. In the first experiment, optimally S-doped crystals demonstrate increase in rectification efficiency for 50-70% to that in GaSe at $\theta = 0°$ without crystal length optimization (Fig.7).

Under the limit pump intensity and appropriate orientation S-doped crystals demonstrated 8.5-15 times higher efficiency. As a rectifier, pure GaSe shown higher THz pulse power to that in ZnTe under pump fluences exceeding 5 mJ/cm^2. Optimally S-doped GaSe demonstrated advantages from fluences over 2 mJ/cm^2 and did not show saturation until pump fluences of over 5 mJ/cm^2. Therefore, S-doped crystals demonstrated serious advantages even in the first experiment that were significantly improved in the following study. Unfortunately, optimization of fs frequency conversion into mid-IR and THz range was not done; on the current time, it is in the progress.

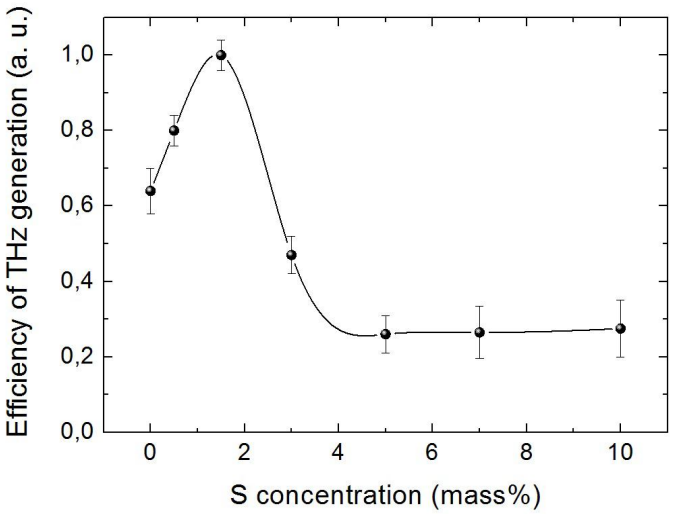

Figure 7. Efficiency of THz generation versus S-doping achieved in the first experiment.

5. CONCLUSION

During the last decade design of top S-doped GaSe syntheses and growth technology is completed. New methods for characterization of physical properties of grown high optical quality crystals are proposed that allowed identification and selection of optimally doped crystals. Frequency conversion of fs pulses into 6.5-35 μm and into 0.2-4.5 THz is realized. S-doped crystals demonstrated advantages from 50-70% in the first experiments up to 8.5-15 times in the following experiments depending on experimental conditions. Optimization of the frequency conversion efficiency seems to be a prospective way in design of high power mid-IR and THz range frequency tunable sources.

6. ACKNOWLEDGMENT

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