Ln$_3$GaS$_6$ (Ln = Dy, Y): new infrared nonlinear optical materials with high laser induced damage thresholds†

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Two new ternary rare earth chalcogenides, Dy$_3$GaS$_6$ (1) and Y$_3$GaS$_6$ (2), are reported here. They both crystallize in the orthorhombic space group Cmc$_2$$_1$ (no. 36). Both are synthesized in pure phase and show phase-matchable second harmonic generation (SHG) of about 0.2 and 0.5 times, respectively for 1 and 2, as strong as that of KTiOPO$_4$ (KTP) based on the powder SHG measurement at the wavelength of 1910 nm. They possess high powder laser induced damage thresholds (LIDTs), respectively, about 14 and 18 times that of AgGaS$_2$ (AGS) based on the powder LIDT measurements under 1064 nm laser irradiation. They both exhibit wide transparency in the IR region (2.5–25 μm). It is believed that the title compounds are new candidates for nonlinear optical (NLO) materials in the IR region. To gain further insights into the NLO and LIDT properties of 1 and 2, the calculations of second-order NLO susceptibility and lattice energy density (LED) were also performed to explain their SHG efficiencies and high LIDTs.

1. Introduction

The generation of high power lasers tunable in the range of 3–20 μm, especially in the regions of 3–5 and 8–14 μm that are known to be two atmospheric transparent windows, has become the focus of the IR laser research. Although new chalcogenide-based nonlinear optical (NLO) materials used for the generation of lasers in IR region have been continuously found, excellent NLO crystals for the IR region are less known. Many current IR NLO crystals such as AgGaS$_2$, AgGaSe$_2$, ZnGeP$_2$ and so on, suffer from either low laser damage threshold or difficulty of crystal growth. The search for new IR NLO crystals has become one of the greatest challenges in this field.

Ternary rare earth series chalcogenides Ln/B/C (Ln = Sc, Y, La–Lu; B = Al, Ga, In; C = S, Se, Te) are less studied. Up to now, only five ternary Ln/Ga/S compounds are reported: EuGa$_5$S$_4$ (orthorhombic, Fddd)$^5$, YbGa$_5$S$_4$ (orthorhombic, Fddd)$^6$, α-LaGaS$_3$ (monoclinic, P2$_1$/c)$^7$, β-LaGaS$_3$ (orthorhombic, Pna2$_1$)$^8$ and Er$_3$GaS$_6$ (orthorhombic, Cmc$_2$$_1$)$^9$, among which only two compounds are non-centrosymmetric and the reports were just mainly focused on the syntheses and structures.

2. Experimental

2.1. Syntheses

The following reagents were used as obtained: Dy$_2$O$_3$ (99%), Y$_2$O$_3$ (99%), Ga$_2$O$_3$ (99.999%), S (99.999%), B (99.99%). Polycrystalline samples of Ln$_3$GaS$_6$ (Ln = Y, Dy) were synthesized by solid-state reaction techniques.$^{16}$ A mixture of Dy$_2$O$_3$/Y$_2$O$_3$, Ga$_2$O$_3$, B, and S in the molar ratio of 3 : 1 : 8 : 12 was ground and pressed into pellets, then loaded into silica tubes. The tubes were evacuated to $1 \times 10^{-3}$ Torr and sealed using an oxyhydrogen flame. The tubes were placed into a computer-controlled furnace and heated to 950 °C in 72 h, kept at that temperature for 72 h and cooled to 400 °C over 7 days.

The phase purity was checked by PXRD. The measured powder X-ray diffraction patterns are in agreement with the
simulated patterns based on the single crystal structures of the title compounds, showing that no impurities were observed (Fig. S1†). They are stable in an ambient air environment for several months.

2.2. Single-crystal structure determination

For 1 and 2, single crystals with dimensions of $0.18 \times 0.16 \times 0.15$ and $0.19 \times 0.15 \times 0.13$ mm$^3$, respectively, were mounted on glass fibers for single-crystal XRD analysis. The measurements were performed on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. The intensity data sets were collected with an omega scan technique and reduced using CrystalClear software.\(^{17}\)

The structures of 1 and 2 were solved by direct methods and refined by full-matrix least-squares techniques on $F^2$ with anisotropic thermal parameters for all atoms. All of the calculations were performed with the Siemens SHELXL version 5 package of crystallographic software.\(^{18}\) The formulas take collectively into account crystallographically refined compositions and requirements of charge neutrality. Relevant crystallographic data and details of the experimental condition for 1 and 2 are summarized in Table 1. Atomic coordinates and selected interatomic distances are reported in Table S1 in the ESI.\(^{†}\)

2.3. Materials and methods

All starting materials were analytical grade from commercial sources and used without further treatment. The powder X-ray diffraction (PXRD) data were collected on an automated Rigaku MiniFlex II X-ray diffractometer equipped with a diffracted monochromator set for Cu-K$_\alpha$ ($\lambda = 1.5418$ Å) radiation.

The data were taken in the 2$\theta$ range of 5°–65° with a scan step width of 0.02° and a fixed scan speed 5° min$^{-1}$. The optical transmission spectra in the mid-IR region were run on a Perkin-Elmer Spectrum One FT-IR spectrophotometer in the range of 4000–400 cm$^{-1}$. The diffuse reflectance spectra were recorded on a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrometer equipped with an integrating sphere in the wavelength range of 190–2500 nm. A BaSO$_4$ plate was used as a reference, on which the finely ground powders of the samples were coated. The absorption spectra were calculated from reflection spectra using the Kubelka-Munk function: $a/S = (1 - R)^2/2R$, in which $a$ was the absorption coefficient, $S$ was the scattering coefficient, and $R$ was the reflectance.\(^{19}\)

2.4. Second harmonic generation (SHG) measurements

The NLO efficiencies of the title compounds were investigated using a modified Kurtz-Perdue powder technique using 1910 nm laser radiation.\(^{20}\) Powder samples of 1 and 2 were ground and sieved into several distinct particle size ranges $(30–50, 50–75, 75–100, 100–150, 150–200, and 200–300$ μm) for the SHG phase-match measurements. As AgGaS$_2$ (AGS) was damaged in 5 seconds under the radiation of the 1910 nm laser, a sample of KTiOPO$_4$ (KTP) $(200–300$ μm) was prepared as a reference material since it has a higher LIDT. All of the samples were pressed between glass microscope cover slides and secured in 1 mm-thick plastic holders containing an 8 mm-diameter hole. The doubled frequency signals (955 nm) were detected by an Andor’s DU420A-BR-DD CCD after the mixed signals passed through the monochromator.

2.5. Powder laser induced damage threshold (LIDT) measurements

As the international standard of ISO 21254-2:2011 is suitable for the LIDT measurements of large single crystals and not suitable for that of polycrystalline powder samples, an easy method, single pulse powder LIDT measurement method, was proposed to evaluate the powder LIDT for new NLO materials. Commercial AGS was used as the reference. The title compounds and AGS were sieved into the same particle size range (75–150 μm) and pressed between glass microscope cover slides. The samples were located along the optical path of the laser, 260 mm away from the focusing lens with focal length of 200 mm, and radiated by the focused high-power 1064 nm laser beam with pulse width $\tau_p$ as 8 ns. The focused spot diameter is about 2 mm. They were observed under an optical microscope once a single pulse radiation passed, and the output power of the laser beam was increased until damage spot was observed. Then the damage laser power was marked and the area of the damage spot was measured to derive the LIDT value of the sample. The power of laser beam was measured by a Nova II sensor display with a PE50-DIF-C energy sensor. The damage spot was measured by a vernier caliper.

2.6. Computational procedures

The calculation models for 1 and 2 were built directly from their crystallographic data determined by single-crystal X-ray
diffraction analysis. The electronic structure calculations based on density functional theory (DFT) were performed utilizing the Vienna *ab initio* simulation package (VASP).

The generalised gradient approximation (GGA) was chosen as the exchange-correlation functional and a plane wave basis with the projector-augmented wave (PAW) potentials was used. The plane-wave cutoff energy of 360 and 295 eV, respectively for 1 and 2, and the threshold of 10−5 eV were set for the self-consistent-field convergence of the total electronic energy. The electronic configurations for Dy, Y, Ga and S were 4f105s25p66s2, 4d104s24p1 and 3s23p4, respectively. And the numerical integration of the Brillouin zone was performed utilizing 9 × 9 × 9 Monkhorst-Pack *k*-point meshes for both compounds. The Fermi level (Em = 0 eV) was selected as the reference.

More than 101 and 99 empty bands were used in optical property calculations and scissors operators of 0.83 and 0.77 were applied for 1 and 2, respectively. Complex dielectric function ε(ω) = ε1(ω) + iε2(ω) were calculated, of which the imaginary part ε2(ω) generated other optical constants via the Kramers-Kroning transform. The static and dynamic second-order nonlinear susceptibilities χ(2)(−ω,ω,ω) were calculated based on the so-called length-gauge formalism by Aversa and Siipe.

The calculations of lattice energies for 1, 2 and AGS were carried out using a computer with the MADEL program attached to the RIETAN powder X-ray Rietveld analysis program. This program employs the EWALD method.

### 3. Results and discussion

#### 3.1. Syntheses

Other than reactions of pure elements or corresponding metal sulfides in conventional solid-state synthesis method, we employed boron–sulfur–metallic oxide reactions to obtain target products in order to avoid the high cost of Ga, Dy, and their sulfides and difficulty to operate owing to the low melting point of Ga element. The by-product B2O3 could be removed by ultrasonic cleaning with distilled water because of its water-solubility. So the pure phase of both compounds could be obtained and their purities were confirmed in a powder X-ray diffraction (XRD) study (Fig. S1†).

#### 3.2. Crystal structure descriptions

Compounds 1 and 2 crystallized in the same space group Cmc21. We can just take compound 1 as an example to show the structure characteristics. As plotted in Fig. 1a, there are two crystallographically unique Dy atoms and one unique Ga atom in the asymmetric unit of 1. The atom Dy1 is coordinated with seven S atoms to form a monocapped triangular prism with the Dy–S bond distances ranging from 2.671(6) to 2.952(6) Å, while the atom Dy2 is in a similar slightly distorted monocapped triangular prism with the Dy–S bond distances ranging from 2.723(6) to 3.001(8) Å. The Ga atom is bonded by four S atoms to form a distorted tetrahedron with the Ga–S bond distances ranging from 2.266(8) to 2.329(8) Å. Because there is no S–S bond in the structure, the oxidation states of Dy, Ga, and S can be assigned to 3+, 3+, and 2−, respectively. The dipole moments of these three polyhedral in the asymmetric unit are calculated using a bond-valence approach proposed by Poeppelmeier et al., and their directions are marked in Fig. 1a. The arrangements of three polyhedral and their dipole moments in unit cell are shown in Fig. 1b–d. As is shown, the dipole moments of the Ga tetrahedra are approximately parallel and summed up to about −10.31 Debye in the direction of negative *c* axis in the unit cell of 1 (Fig. 1b). The dipole moments of the Dy1 polyhedral cancel out completely in the direction of *a* axis, leaving the summed dipole moments (about 4.71 Debye) assigned in the direction of *c* axis (Fig. 1c). Similarly, the dipole moments of the Dy2 polyhedra cancel out completely in the direction of *b* axis, resulting in the summed dipole moments (about −2.57 Debye) pointing at the direction of negative *c* axis (Fig. 1d). Consequently, the summed dipole moments for each kind of polyhedra partly offset to produce the net dipole moment (about −8.17 Debye) of unit cell in the direction of negative *c* axis. Finally, the unit cells are assigned in a parallel manner to constructively generate the macroscopic dipole moment of the crystal in the direction of negative *c* axis for 1, which is fundamental for the spontaneous polarization (about 2.99 × 10−2 C m−2) of 1 to produce the pyroelectric effect.

The analysis result of the dipole moments above is consistent with the space group Cmc21. The existence of *m* and *c* symmetry planes in the directions of *a* and *b* axes leads to the offset of the dipole moments in both directions. Consequently, the compounds crystallized in the space group Cmc21 certainly possess the net dipole moments in the direction of *c* axis.

![Fig. 1](image-url)
3.3. Optical properties

The FT-IR spectra of 1 and 2 show there is no obvious absorption peak in the mid-IR region from 2.5 to 25 μm (Fig. S2†), indicating the transparency edge of 1 and 2 can reach 25 μm, which is comparable with AGS. As shown in Fig. S3† several characteristic absorptions of the Dy3+ transition (6H15/2 → 2S1/2LJ) are observed between 420–480 and 740–1900 nm. The three absorption bands with peaks of 431, 457, and 475 nm are ascribed to the 4f–4f transitions of Dy3+ which originate from the ground state 6H15/2 to 4F11/2 (431 nm), 4I15/2 (457 nm), and 4F9/2 (475 nm). These three less-intense transitions are spin-forbidden transitions (ΔS ≠ 0) between the 6H15/2 ground state and the 6G, 4I and 4F terms. There are six intense absorption bands ranging from 740 to 1900 nm with peaks of 761, 812, 909, 1103 and 1698 nm, which are ascribed to the 4f–4f transitions of Dy3+, and originate from the ground state 6H15/2 to 6F7/2 + 6H5/2 (761 nm), 6F5/2 (812 nm), 6F7/2 + 6H5/2 (909 nm), 6F9/2 + 6H7/2 (1103 nm), 6F11/2 + 6H9/2 (1301 nm), and 6H11/2 (1698 nm). These intense transitions are spin-allowed transitions (ΔS = 0) between the 6H15/2 ground state and the 6F and 6H terms.36 The bands ranging from 1550 to 1900 nm are split into six obvious peaks of 1661, 1680, 1698, 1725, 1750 and 1775 nm, which are due to the ligand field effect to result in the Kremers splitting of the 6H11/2 term of Dy3+. As plotted in Fig. S4† the band gaps could be derived as 2.81 and 2.88 eV, respectively, for 1 and 2. There is no characteristic absorption peak because of the absence of 4f electrons in the wavelength range of 780–2600 nm for 2.

3.4. Second harmonic generation (SHG) measurement

Powder SHG measurements using 1910 nm radiation revealed that compounds 1 and 2 showed SHG signals of approximately 0.2 and 0.5 times, respectively, as strong as that of KTP (d_eff = 14.6 pm V⁻¹) with the same particle size range of 200–300 μm. The weaker SHG signal of 1 compared with that of 2 could be ascribed to the slight absorption of 1 at the frequency-doubled wavelength of 955 nm (Fig. S3†). It is well known that the measured SHG signal intensity by the Kurtz and Perry powder method is proportional to the square of the SHG coefficient d_eff and the second-order susceptibility χ(2)eff is twice of the SHG coefficient d_eff, so the derived second-order susceptibilities χ(2)eff for 1 and 2 are 13.06 and 20.65 pm V⁻¹, respectively.

As shown in Fig. 2, the powder SHG intensities of 1 and 2 rise with the increase of the particle size from 30 to 300 μm, and then tends to be constant. These are typical curves of the type-I phase-matchable materials, which is a necessary characteristic for an NLO material to serve for laser frequency conversion.

3.5. Powder laser induced damage threshold measurement

The measured powder LIDTs of 1, 2 and AGS by the single pulse powder LIDT measurement method above are shown in Table 2. The LIDTs of 1 (79.45 MW cm⁻²) and 2 (103.78 MW cm⁻²) are about 14 and 18 times that of AGS (5.58 MW cm⁻²), respectively, indicating that both compounds may be good candidates for high-power NLO application.

The intense laser beams result in a variety of damages in crystals, like defects, cracks, melt, sublimation, decomposition of compounds, and so on. These damages always happen with destruction of the original crystal lattice. So it is rational to expect that the LIDT is related to the lattice stability of compounds. Lattice energy (LE) can be employed to evaluate the lattice stability of compounds. So lattice energies (LEs) and lattice energy densities (LEDs) of 1, 2 and AGS are calculated and listed in Table 2. It is found that the sequence of LEDs is consistent with that of the LIDTs for three compounds, which demonstrates the corollary above. It could be concluded

![Fig. 2](Image 340x479 to 514x729)

**Fig. 2** Dependence of SHG intensities on the particle sizes for 1 (a) and 2 (b).
that LED is a critical factor to influence the LIDTs of NLO compounds. So we can roughly compare the LIDTs of new compounds by the simple calculation of LEDs.

Of course, considering that the process of inducing damage in material by laser is complicated, the LIDT of NLO materials is also influenced by other factors such as heat capacity, heat conductivity and so on, in addition to LED of compounds.

3.6. Electronic structures calculations

The calculated band structures of 1 and 2 along with high symmetry points of the first Brillouin zone are plotted in Fig. 3. The lowest energy (1.98 and 2.11 eV, respectively for 1 and 2) of conduction bands (CBs) is localized at the Y point and the highest energy (0.0 eV for 1 and 2) of valence bands (VBs) is localized at the G point. Accordingly, compounds 1 and 2 show semiconducting character with indirect band gaps of 1.98 and 2.11 eV, which are smaller than the experimental values (2.81 and 2.88 eV) owing to the inaccurately description of the eigenvalues of the electronic states in GGA. The bands can be assigned according to the total and partial density of states as plotted in Fig. 4. For 1, the VBs between the energy level −5.0 eV and the Fermi level (0.0 eV) are mostly formed by the S-3p state mixing with small amount of Dy-4d and Dy-4f states, while the CBs between 2.0 and 6.0 eV are almost a contribution from the Dy-4d and Dy-4f states hybridized with a small amount of S-3p state. Accordingly, the intrinsic absorptions of 1 can be ascribed to the charge transitions from S-3p to Dy-4d states. Similarly, the optical intrinsic absorptions of 2 can be mainly ascribed to the charge transitions from S-3p to Y-4d states.

3.7. Optical properties calculations

The linear optical properties were examined according to the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The energy dependence of the real part $\varepsilon_1$ and imaginary part $\varepsilon_2$ are displayed in Fig. 5 and S6.† Because of the nonmetallic characteristics of the title compounds, the imaginary part $\varepsilon_2(\omega)$ is used to describe the interband electronic transitions between the occupied and unoccupied states. The average values of the polarized zero-frequency dielectric constants $\varepsilon_{\text{ave}}^{\text{pol}}(0)$ are 7.01 and 7.02 for 1 and 2, respectively. The refractive index $n(\omega)$, birefringence ($\Delta n$), absorption coefficient $k(\omega)$ and reflectivity $R(\omega)$ were also calculated. As shown in Fig. S7,† the static refractive indexes are both 2.65 for 1 and 2. As plotted in Fig. S10,† the static birefringence ($\Delta n$) values are found to be 0.066 and 0.068 for 1 and 2, which are smaller than that of KTP (0.083). The $\Delta n$ values at 1910 nm (0.649 eV) are about 0.068 and 0.069 for 1 and 2, respectively. As both compounds are experimentally phase-matchable at 1910 nm, we can derive that they can implement the phase-match behavior when the $\Delta n$ value are around 0.068 and 0.069, implying they may be phase-matchable in the wavelength range of 1910–∞ nm which includes the mid/far IR ranges.

For the space group of 1 and 2 is Cmc21, the rank $n$ second-order susceptibility tensor $\chi^{(n)}$ in mm2 symmetry has 5 nonvanishing elements: $X_{157}$, $X_{234}$, $X_{312}$ and $X_{333}$, three of which remain under the assumption of Kleinman symmetry ($X_{33} = X_{157}$, $X_{32} = X_{234}$). As shown in Fig. 5, the calculated $d_{31}$, $d_{32}$ and $d_{33}$ coefficients, half the three independent second-order tensors $X_{311}$, $X_{312}$ and $X_{333}$ are 13.93, 18.88 and 23.49 pm V$^{-1}$ for 1, and 12.93, 17.16 and 20.85 pm V$^{-1}$ for 2 at the wavelength of 1910 nm (0.649 eV). The $d$ values of 1 are a little larger than
two regions, −5–0 and 2.5–10 eV. The region of −5–0 eV is dominated by S-3p, Dy-4d and Dy-4f states, whereas another region is mainly contributed from Dy-4d and Dy-4f states (Fig. 4). The situation of 2 is similar to that of 1. Consequently, the SHG responses are mainly ascribed to the electronic transitions from S 3p states to Ln-4d and Ln-4f states.

4. Conclusions

The new ternary rare earth chalcogenides, 1 and 2, can be synthesized on a large scale in pure phase by solid state reactions, showing comparatively large phase-matchable SHG effects of 0.2 and 0.5 times as strong as that of KTP and very high LIDTs of about 14 and 18 times as strong as AGS for 1 and 2, respectively. It is believed that both compounds are new candidates for NLO materials in the IR region. The large SHG efficiencies and high LIDTs of 1 and 2 were explained by the calculations of second-order NLO susceptibility and LED. In addition, an easy-to-operate method, namely, single pulse powder LIDT measurement method, was proposed to evaluate the relative LIDT value of new NLO compounds, which can be easily adopted by other groups in the future. The LED can be employed to evaluate the LIDTs of new compounds qualitatively.

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Notes and references
