

## *Supporting Information*

### **Monoclinic gallium selenide: an AgGaS<sub>2</sub>-type structure variant with balanced infrared nonlinear optical performance**

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#### **Experimental Section**

**Synthesis and Analyses.** The title compound was synthesized using a modified Lübbers' method.<sup>1</sup> All raw materials were used directly and the target product was obtained via a solid-state method under high temperature. The raw materials were Ga (99.99 %), Se (99.999 %), and KI (99 %). The molar ratio of Ga/Se was slightly lower than 2/3, and their total mass was 500 mg, and additional 500 mg KI was used as the flux. The mixture was grounded into fine powder in an agate mortar and pressed into one pellet, which was then sealed into an evacuated quartz tube with the vacuum degree of  $1 \times 10^{-4}$  torr. The quartz tube was heated in the muffle furnace from room temperature to 573 K in 5 h and equilibrated for 5 h, followed heated to 873 K in 5 h and maintained for 200 h, finally quenched with water. The product was washed using distilled water more than 3 times and the orange block single crystals were obtained. The sizes of single-crystals are observed by a Zeiss scanning electron microscope (Fig. S1), and the purity was confirmed by powder X-ray diffraction analysis. The PXRD pattern was collected with a Bruker D8 Advance diffractometer at 40 kV and 100 mA for Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) with a scan speed of 5 °/min at room temperature. The simulated pattern was produced using the Mercury v3.8 program provided by the Cambridge Crystallographic Data Center and single-crystal reflection data. The PXRD pattern of Ga<sub>2</sub>Se<sub>3</sub> (Fig. S2) corresponds well with the simulated one, indicating a pure phase.

**Structure Determination.** The intensity data set of Ga<sub>2</sub>Se<sub>3</sub> is collected on a Bruker D8 QUEST X-ray diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure is solved by Direct Methods and refined by full-matrix least-squares techniques on  $F^2$  with anisotropic displacement parameters for all atoms. All the calculations are performed with the Olex2 crystallographic software. The final refinements included anisotropic displacements parameters for all atoms and a secondary extinction correction.<sup>2</sup> The cif document is also deposited with the CCDC number of 1935068.

**Infrared and UV–Vis–NIR Diffuse Reflectance Spectroscopies.** The IR spectrum was recorded by using a TENSOR27 FT-IR spectrophotometer in the range of 4000–400 cm<sup>-1</sup>. Powdery sample was pressed into one pellet with KBr. The diffuse reflectance spectrum was recorded at the room temperature on a computer-controlled Cary 5000 UV–Vis–NIR spectrometer equipped with an integrating sphere in the wavelength range of 300–1700 nm. A BaSO<sub>4</sub> plate was used as a reference, on which the finely ground powdery sample was coated. The absorption spectrum was calculated from reflection spectrum by the Kubelka-Munk function.<sup>3</sup>

**SHG and Powder LIDT Measurements.** SHG measurements on powdery crystalline sample of Ga<sub>2</sub>Se<sub>3</sub> were performed using a modified Kurtz-Perry powder method,<sup>4</sup> and 2.1  $\mu$ m laser was employed as the radiation light. The powder sample was ground and sieved into several distinct particle size ranges of 25~45, 45~75, 75~100, 100~150 and 150~210  $\mu$ m for the SHG phase-matchable measurements. AgGaS<sub>2</sub> (AGS) crystals with a uniform particle size range served as the standard. The SHG signals at 1050 nm were collected in a reflection geometry from the excitation surface and focused into a fiber optic bundle. The output of the fiber optic bundle was coupled to the entrance slit of a spectrometer, passed through the monochromator, and then detected using an Andor DU420A-BR-DD CCD detector.

The single-pulse measurement method was used to evaluate the LIDTs of Ga<sub>2</sub>Se<sub>3</sub> and AGS. The three crystalline samples with the same size range (50~75  $\mu$ m) were selected and pressed into glass microscope cover slides. The samples were radiated by 1064 nm laser with a pulse width  $\tau_p$  of 10 ns in a 1 Hz repetition. The measurements were carried out under an optical microscope once single-pulse radiation was passed, and the laser power increased until the damaged spot was observed. Then, the laser power was marked, and the area of the damaged

spot was measured as the damage threshold parameters of the sample. The laser beam power was monitored by a Nova II sensor display with a PE50-DIT-C energy sensor. The damaged spot was measured using a Vernier caliper.

**Calculation details.** The calculation model was built from the single-crystal diffraction data of Ga<sub>2</sub>Se<sub>3</sub>. The calculations including band structure, density of states (DOS), and optical properties were carried out using CASTEP module in Material Studio software.<sup>5</sup> The exchange-correlation function GGA (generalized gradient approximation) was chosen and a plane wave basis with the PAW (projector-augmented wave) potentials was used. The plane-wave cutoff energy was 330 eV, and the threshold of 10<sup>-5</sup> eV was set for the self-consistent-field convergence of the total electronic energy. The electronic configurations for Ga and Se were 4s<sup>2</sup>4p<sup>1</sup> and 4s<sup>2</sup>4p<sup>4</sup>, respectively. The numerical integration of the Brillouin zones were performed using 4 × 2 × 4 Monkhorst–Pack *k*-point meshes and the Fermi level at 0 eV were chosen as the reference.

The optical properties described in terms of the complex dielectric function  $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$  were calculated.  $\varepsilon_1(\omega)$  and  $i\varepsilon_2(\omega)$  represent the real and imaginary parts of dielectric function, respectively. These two parts can be obtained using eqs. 1 and 2, respectively.<sup>6,7</sup>

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (1)$$

$$\varepsilon_2(\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{K,V,C} |\langle \psi_K^C | \hat{u} \cdot r | \psi_K^V \rangle|^2 \delta(E_K^C - E_K^V - E) \quad (2)$$

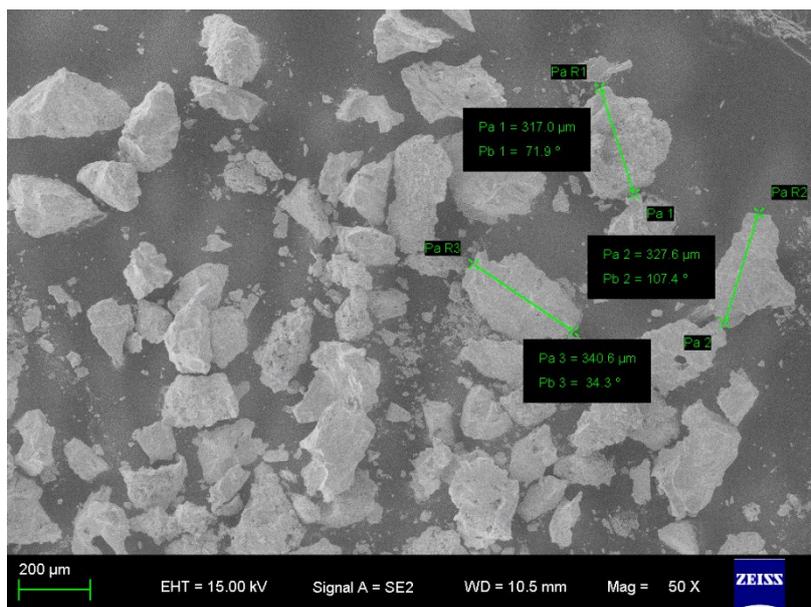
$\varepsilon_2(\omega)$  can be used to generate other optical constants using the Kramers-Kronig transform.<sup>8,9</sup> In eq. 2,  $\delta(E_K^C - E_K^V - E)$  denotes the energy difference between the conduction and valence bands at the *k* point with absorption energy *E*,  $\hat{u}$  represents the polarization of the incident electric field,  $\Omega$  is the primitive cell volume, *e* is the electric charge, and  $\Psi_K^C$  and  $\Psi_K^V$  are the vectors defining the conduction and valence band wave functions at *k*, respectively. The first-order nonresonant susceptibility at the low-frequency region is given by  $x^{(1)}(\omega) = \varepsilon_1(\omega) - 1$ , and the second-order susceptibilities can be expressed in terms of the first-order susceptibilities as follows:<sup>10,11</sup>

$$\chi_{ijk}^{(2)}(\omega_3, \omega_1, \omega_2) = \frac{ma}{N^2 e^3} \chi_{ii}^{(1)}(\omega_3) \chi_{jj}^{(1)}(\omega_1) \chi_{kk}^{(1)}(\omega_2) \quad (3)$$

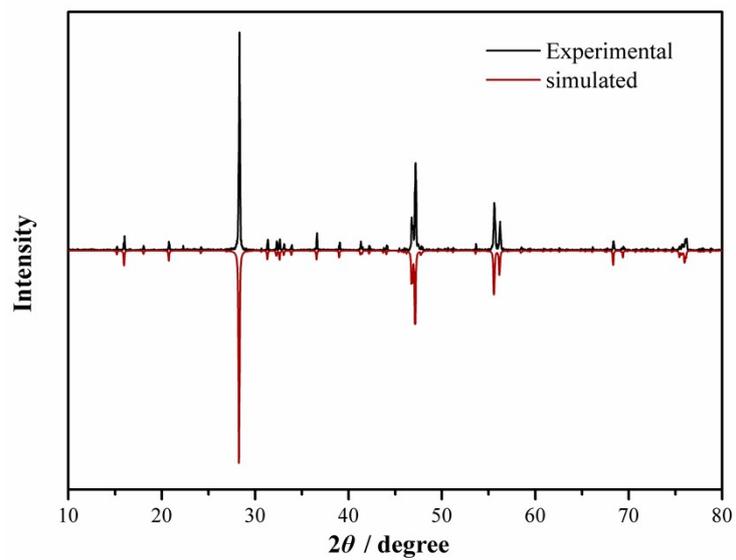
In eq. 3,  $m$ ,  $e$ , and  $N$  are the electron mass, electron charge, and number density of the atoms, respectively, and the parameter  $a$  representing the nonlinear response.

Refractive index  $n$  was obtained using the below equation,

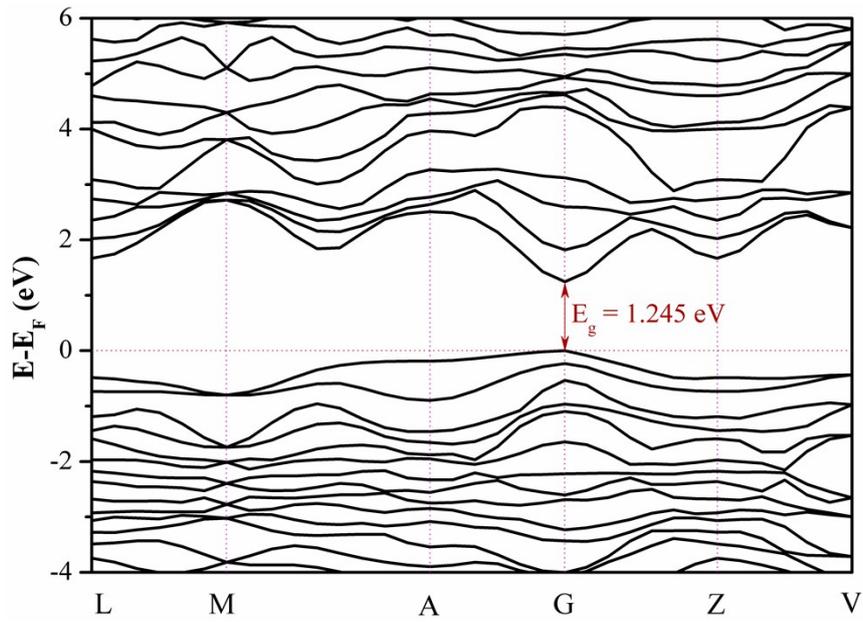
$$n(\omega) = \sqrt{\frac{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) + \varepsilon_1(\omega)}{2}} \quad (4)$$



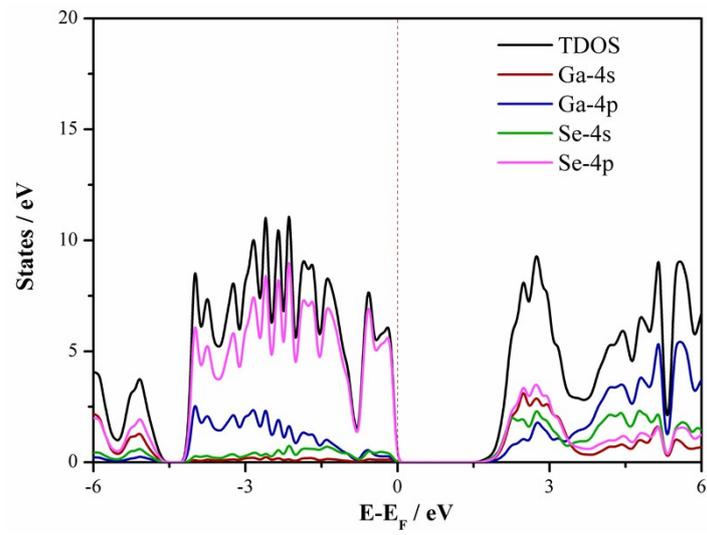
**Fig. S1** SEM image of the as-prepared crystals of monoclinic Ga<sub>2</sub>Se<sub>3</sub>.



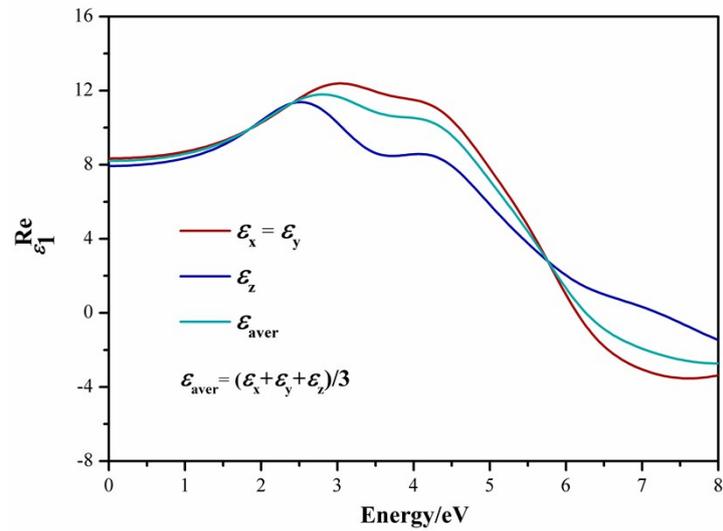
**Fig. S2** Powder X-ray diffraction pattern of Ga<sub>2</sub>Se<sub>3</sub>. The simulated one is obtained using the single-crystal structure data of monoclinic Ga<sub>2</sub>Se<sub>3</sub>.



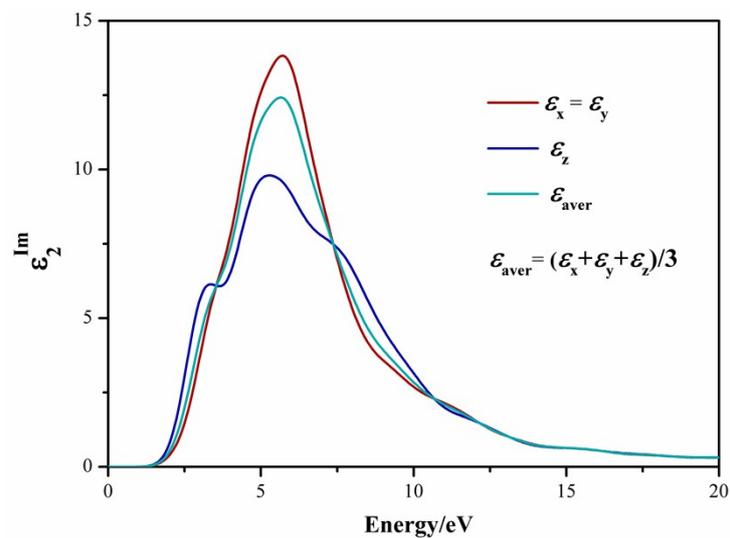
**Fig. S3** Calculated band structure of Ga<sub>2</sub>Se<sub>3</sub>. The Fermi level is chosen as the energy reference at 0 eV and the band gap is calculated to be 1.245 eV.



**Fig. S4** Calculated density of states (DOS) of Ga<sub>2</sub>Se<sub>3</sub>. The Fermi level is chosen as the energy reference at 0 eV.



(a)



(b)

**Fig. S5** Calculated real and imaginary parts of optical dielectric functions of Ga<sub>2</sub>Se<sub>3</sub> (Re: real part; Im: imaginary part).

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