Supplemental Document

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Recalibration of the nonlinear optical coefficients of $BaGa_4Se_7$ crystal using second-harmonic-generation method: supplement

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Supplementary material for
Recalibration of the nonlinear optical coefficients of $BaGa_4Se_7$ crystal using second-harmonic-generation method

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1. Expression of d_{eff} along arbitrary direction in BGSe crystal

For BGSe crystal, after considering Kleimann symmetry, there are still six independent NLO coefficients, and the NLO coefficient matrix is as follows:

$$d_{\mathrm{in}} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & 0 & 0 \\ d_{15} & d_{24} & d_{33} & d_{23} & 0 & 0 \end{bmatrix} \tag{S1}$$

In anisotropic crystals, for a light wave with a unit vector of $\boldsymbol{k_0}$ in the wave vector direction, the relationship between the electric displacement vector $\boldsymbol{D}$ and the electric field intensity $\boldsymbol{E}$ is as follows:

$$\boldsymbol{D} = n^2[\boldsymbol{E} - \boldsymbol{k_0}(\boldsymbol{k_0} \cdot \boldsymbol{E})] \tag{S2}$$

where n represents refractive index. From the Eq. (S2), there is

$$\begin{cases} D_x = n^2[E_x - k_{0x}(\boldsymbol{k_0} \cdot \boldsymbol{E})] \\ D_y = n^2[E_y - k_{0y}(\boldsymbol{k_0} \cdot \boldsymbol{E})] \\ D_z = n^2[E_z - k_{0z}(\boldsymbol{k_0} \cdot \boldsymbol{E})] \end{cases} \tag{S3}$$

For biaxial crystals, the relationship between $\boldsymbol{D}$ and $\boldsymbol{E}$ on the optical principal axis is

$$\begin{cases} D_x = \varepsilon_x E_x = n_x^2 E_x \\ D_y = \varepsilon_y E_y = n_y^2 E_y \\ D_z = \varepsilon_z E_z = n_z^2 E_z \end{cases} \tag{S4}$$

Substitute the Eq. (S4) into the Eq. (S3), the sorting formula can be obtained as

$$\begin{cases} D_x = k_{0x}(\boldsymbol{k_0} \cdot \boldsymbol{E})/(n_x^{-2} - n^{-2}) \\ D_y = k_{0y}(\boldsymbol{k_0} \cdot \boldsymbol{E})/(n_y^{-2} - n^{-2}) \\ D_z = k_{0z}(\boldsymbol{k_0} \cdot \boldsymbol{E})/(n_z^{-2} - n^{-2}) \end{cases} \tag{S5}$$

From the Eqs. (S4) and (S5), the followed equations can be deduced

$$\begin{cases} [n_x^2 - n^2(1 - k_{0x}^2)]E_x + n^2 k_{0x} k_{0y} E_y + n^2 k_{0x} k_{0z} E_z = 0 \\ n^2 k_{0x} k_{0y} E_x + [n_y^2 - n^2(1 - k_{0y}^2)]E_y + n^2 k_{0y} k_{0z} E_z = 0 \\ n^2 k_{0x} k_{0z} E_x + n^2 k_{0z} k_{0y} E_y + [n_z^2 - n^2(1 - k_{0z}^2)]E_z = 0 \end{cases} \tag{S6}$$

Under polar coordinates, the unit wave vector in arbitrary direction (θ, ϕ) is $\boldsymbol{k_0}$ (sinθcosϕ, sinθsinϕ, cosθ**)**. By taking the three principal axis refractive indices $n_x(\omega_j)$, $n_y(\omega_j)$, $n_z(\omega_j)$, the unit wave vector $\boldsymbol{k_0}$, the slow light refractive index $n'(\omega_j)$ and fast light refractive index $n''(\omega_j)$ into the formulae (S6) respectively, the three components of the polarization direction for slow light $\boldsymbol{e}_1(\omega_j)$ and fast light $\boldsymbol{e}_2(\omega_j)$ can be solved as follows:

$$(\boldsymbol{e_1(\omega_j)}) = (\cos\alpha'(\omega_j) \quad \cos\beta'(\omega_j) \quad \cos\gamma'(\omega_j)) \tag{S7}$$

$$(\boldsymbol{e_2(\omega_j)}) = (\cos\alpha''(\omega_j) \quad \cos\beta''(\omega_j) \quad \cos\gamma''(\omega_j)) \tag{S8}$$

where the below relationships are satisfied:

$$cos^2\alpha'(\omega_j) + cos^2\beta'(\omega_j) + cos^2\gamma'(\omega_j) = 1 \tag{S9}$$

$$cos^2\alpha''(\omega_j) + cos^2\beta''(\omega_j) + cos^2\gamma''(\omega_j) = 1 \tag{S10}$$

For type-I phase matching, the fundamental wave is slow light and the SHG wave is fast light, the calculation formulae of effective NLO coefficient d_{eff} is as follows

$$d_{\mathrm{eff}}(\mathrm{I}) = (\cos\alpha''(2\omega) \quad \cos\beta''(2\omega) \quad \cos\gamma''(2\omega))(d_{\mathrm{in}}) \begin{pmatrix} cos^2\alpha'(\omega) \\ cos^2\beta'(\omega) \\ cos^2\gamma'(\omega) \\ 2\cos\beta'(\omega)\cos\gamma'(\omega) \\ 2\cos\alpha'(\omega)\cos\gamma'(\omega) \\ 2\cos\alpha'(\omega)\cos\beta'(\omega) \end{pmatrix} \tag{S11}$$

Taking Eq. (S1) into Eq. (S11), there is:

$$\begin{aligned} d_{eff}(\mathrm{I}) = {} & (2\cos\alpha'(\omega)\cos\gamma'(\omega)\cos\alpha''(2\omega) + cos^2\alpha'(\omega)\cos\gamma''(2\omega))d_{15} + \\ & (2\cos\alpha'(\omega)\cos\beta'(\omega)\cos\alpha''(2\omega) + cos^2\alpha'(\omega)\cos\beta''(2\omega))d_{16} + (cos^2\beta'(\omega)\cos\beta''(2\omega))d_{22} + \\ & (2\cos\beta'(\omega)\cos\gamma'(\omega)\cos\gamma''(2\omega) + cos^2\gamma'(\omega)\cos\beta''(2\omega))d_{23} + \\ & (2\cos\beta'(\omega)\cos\gamma'(\omega)\cos\beta''(2\omega) + cos^2\beta'(\omega)\cos\gamma''(2\omega))d_{24} + (cos^2\gamma'(\omega)\cos\gamma''(2\omega))d_{33} \end{aligned} \tag{S12}$$

Based on the equations (S6)-(S12), for all of the PM angles in Fig. 1, the coefficient of d_{33} (i.e. $cos^2\gamma'(\omega)\cos\gamma''(2\omega)$) is calculated to be smaller than 0.04. It means that the value of d_{33} has little influence on the calculation of d_{eff}. Even if d_{33} is as large as 30 pm/V, the final calculation error will not be greater than 1.2 pm/V.

2. Measuring principle of d_{eff} by second-harmonic-generation method

Under small-signal conditions where the effects of pump depletion are neglected, the SHG output of femtosecond laser pulses can be expressed as follows [1]:

$$W_2 = \frac{8\pi^2|d_{eff}|^2}{\varepsilon_0 c n_1^2 n_2 \lambda^2} \cdot \frac{W_{fund}^2 L}{\alpha A_{eff}} \tag{S13}$$

where W_{fund} and W_2 represent the fundamental and SHG pulse energies respectively, ε_0 represents the vacuum dielectric constant, c represents the speed of light, n_1 and n_2 represent the refractive index of fundamental and SHG waves respectively, λ represents the fundamental wavelength, A_{eff} represents the effective cross section of the fundamental beam, L represents the thickness of the NLO crystal, and α represents the group velocity mismatch (GVM) of the NLO crystal which can be obtained from Eq. (S14) as follow:

$$\alpha = \frac{1}{v_2} - \frac{1}{v_1} \tag{S14}$$

where v_1 and v_2 represent the group velocities of the fundamental and SHG waves respectively, which follow the expression below:

$$v = \frac{c}{n - \lambda \cdot \frac{dn}{d\lambda}} \tag{S15}$$

Above equations show that the conversion efficiency of SHG process is limited by GVM, which describes the temporal walk-off between the fundamental and SHG beams. This walk-off is due to the mismatch of group velocity, which is particularly significant in the femtosecond pulse, and can be ignored in the nanosecond pulse. By taking the SHG experimental data and material parameters of different NLO crystals into the Eq. (S13) respectively, the relative magnitude of their $|d_{\text{eff}}|$ can be determined, in this way the $|d_{\text{eff}}|$ of a new NLO crystal can be obtained by comparison with a mature NLO sample whose $|d_{\text{eff}}|$ has been widely accepted.

In the main text, we used a LBO crystal as the reference sample to calibrate the $|d_{\text{eff}}|$ of different BGSe samples at λ_ω = 2.128 μm. To minimize errors, the LBO sample was prepared with the same parameters as BGSe samples, including being processed along (90°, 34.4°) to perform the same SHG experiment of 2.128 → 1.064 μm, and the same crystal thickness of 2.5 mm.

The Eq. (S13) is a simplified formula to describe the process of SHG in the nonstationary regime ($L >> L_{\text{nst}}$, where $L_{\text{nst}} = \tau/\alpha$, τ is the time duration of the fundamental pulses, and α is the GVM parameter), which applies to the SHG in bulk media with unfocused beams. In this work, we use a beam compression system (ϕ2.5 mm → ϕ1 mm) to increase the intensity of fundamental beam, so the fundamental beam can be seem as approximately parallel. Additionally, the further calculation manifests there is $L > 3L_{\text{nst}}$ for all of the experimental samples, i.e. the nonstationary regime ($L >> L_{\text{nst}}$) is basically satisfied here. Therefore, the Eq. (S13) is applicable to the present SHG experiments.

3. Experimental data and the fitting process of NLO coefficients matrix [d_{in}]

The SHG experimental result were shown in Fig. S1. Fig. S1(a) exhibited the pump and SHG power in the near infrared waveband (λ_ω = 2.128, 1.8 μm), which was obtained from a tuning femtosecond laser (ORPHEUS-HP, Light Conversion

Inc.). Fig. S2(b) exhibited the experimental data in the mid infrared waveband ($\lambda_\omega = 10.6$ μm), which was obtained from a homemade nanosecond CO_2 laser.

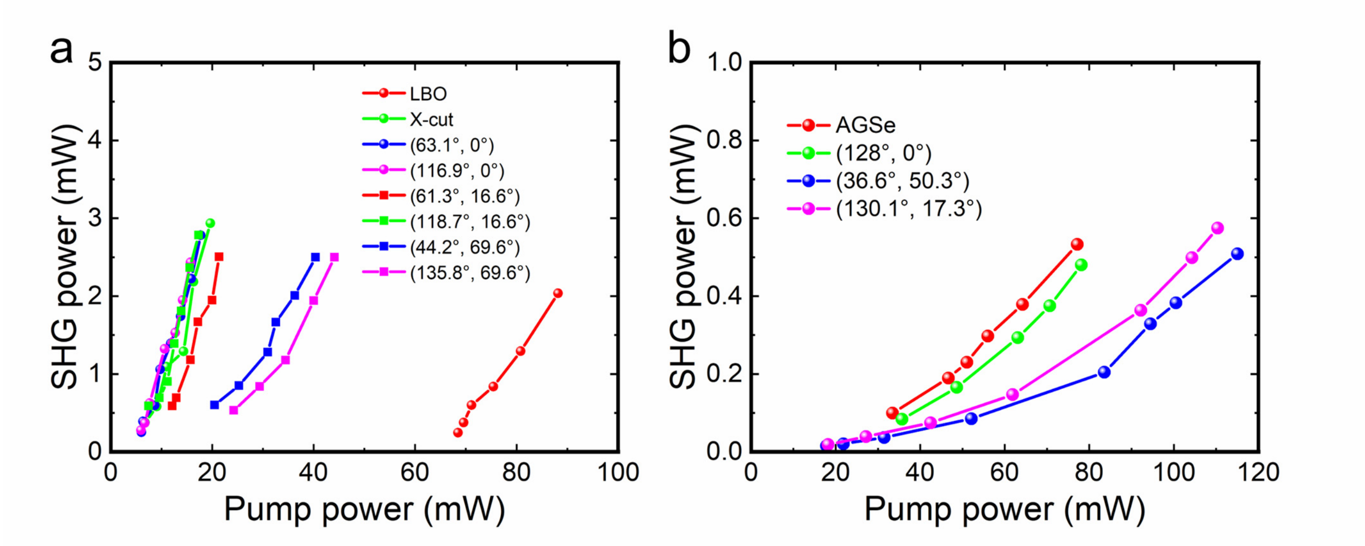

Fig. S1. a. pump and SHG power of BGSe, LBO samples. The data of X-cut BGSe are from the SHG of 1.8 → 0.9 μm, and others are from the SHG of 2.128 → 1.064 μm. b. pump and SHG power of BGSe, AGSe samples for the SHG of 10.6 → 5.3 μm.

Firstly, the SHG experiments of BGSe crystal at 1.8 and 2.128 μm were performed. Simultaneously, the SHG experiment of LBO crystal at 2.128 μm was performed as a reference. The experimental results at low conversion efficiency were plotted in Fig. S1(a). In Eq. (S13), the thickness L and the effective cross section of the fundamental beam $A_{\rm eff}$ of BGSe and LBO crystals are the same. The vacuum dielectric constant and the speed of light are constants, which can be offset in calculation. Therefore, Eq. (S13) can be changed to

$$d_{\rm eff}^2\,(\mathrm{BGSe}) = 0.76^2 \cdot \frac{W_{2,BGSe}}{W_{2,LBO}} \cdot \frac{W_{fund,LBO}^2}{W_{fund,BGSe}^2} \cdot \frac{n_{1,BGSe}^2}{n_{1,LBO}^2} \cdot \frac{n_{2,BGSe}}{n_{2,LBO}} \cdot \frac{\lambda_{BGSe}^2}{\lambda_{LBO}^2} \cdot \frac{\alpha_{BGSe}}{\alpha_{LBO}} \tag{S16}$$

With the LBO sample as reference ($d_{\rm eff}$ = 0.76 pm/V), and taking the SHG experimental results and crystal parameters into equation (S16), the $d_{\rm eff}$ value of each BGSe sample was obtained by comparison. For the X-cut BGSe crystal, there is $d_{\rm eff} = |d_{23}|$, which is measured to be 22.8 pm/V at $\lambda_\omega = 1.8$ μm, and the corresponding value at $\lambda_\omega = 2.128$ μm is 22.1 pm/V when the Miller's rule is applied. In the XZ principal plane of BGSe ($\phi = 0$), the formula of effective nonlinearity can be written as follows:

$$d_{\rm eff} = d_{16}cos^2\theta + d_{23}sin^2\theta \tag{S17}$$

The $d_{\rm eff}$ value of the (63.1°, 0°) and (116.9°, 0°) directions are the same, which is 24.3 pm/V, as demonstrated by the similar SHG experimental results. Because the SHG effects of (63.1°, 0°) and (116.9°, 0°) directions are stronger than that of X direction, the sign of d_{23} and d_{16} should be the same; thus, the absolute value of d_{16} is determined to be 31.5 pm/V from Eq. (S17), which is larger than d_{23}. For convenience, the sign of d_{23} and d_{16} is set to be positive hereafter, and the signs of the other nonlinear coefficients are based on this setting. As mentioned above, because the influence of d_{33} on $d_{\rm eff}$ is very small, and d_{33} was not detected before [2], the value of d_{33} is set to be zero.

The BGSe crystal belongs to the monoclinic point group m (X//b), and there are six non-zero and independent d_{in} coefficients when the Kleinman symmetry is followed, which are d_{15} (=d_{31}), d_{16} (=d_{21}), d_{22}, d_{23} (=d_{34}), d_{24} (=d_{32}), and d_{33}. The corresponding [d_{in}] matrix is the Eq. (S1). The $|d_{eff}|$ of remaining four samples with directions of (61.3°, 16.6°), (118.7°, 16.6°), (44.2°, 69.6°), and (135.8°, 69.6°) are calibrated to be 19.0, 20.4, 7.5, and 6.8 pm/V respectively. Using these $|d_{eff}|$ values, as well as d_{23} = 22.1 pm/V, d_{16} = 31.5 pm/V, d_{33} = 0, the other three d_{in} coefficients can be fitted out, which are d_{15} = 0.3 pm/V, d_{22} = -13.5 pm/V, and d_{24} = 0.7 pm/V respectively. During the fitting process, all positive and negative signs possibilities of d_{15}, d_{22}, and d_{24} have been examined. Among the eight possibilities, the above option is the only one that can coincide with all the experimental results of $|d_{eff}|$ values. To sum up, with the phase-matched SHG method, a new [d_{in}] matrix of BGSe crystal at λ_ω = 2.128 μm was obtained as follows:

$$d_{\text{in}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0.3 & 31.5 \\ 31.5 & -13.5 & 22.1 & 0.7 & 0 & 0 \\ 0.3 & 0.7 & 0 & 22.1 & 0 & 0 \end{bmatrix} \tag{S18}$$

Subsequently, the SHG experiments of BGSe and AGSe crystals at 10.6 μm were performed, in which AGSe was the reference sample. The experimental results at low conversion efficiency were plotted in Fig. S1(b). Because all of the samples have the same transmission length and fundamental wavelength, and the pulse duration is at the nanoseconds level, the factors of L, λ, and α can be omitted when the Eq. (S13) is used to handle the experimental data. Therefore, the Eq. (S13) can be changed to

$$d_{\text{eff}}^2\,(\text{BGSe}) = 27^2 \cdot \frac{W_{2,BGSe}}{W_{2,AGSe}} \cdot \frac{W_{fund,AGSe}^2}{W_{fund,BGSe}^2} \cdot \frac{n_{1,BGSe}^2}{n_{1,AGSe}^2} \cdot \frac{n_{2,BGSe}}{n_{2,AGSe}} \tag{S19}$$

The SHG experimental results of Fig. S2(b) were substituted into the Eq. (S19), and using the AGSe crystal as a reference (d_{eff} = 27 pm/V), the d_{eff} values of the (128°, 0°), (130.1°, 17.3°), and (36.6°, 50.3°) BGSe crystals were measured to be 23.5, 16.9, and 15.0 pm/V, respectively. Considering Miller's rule, the matrix (S18) at λ_ω = 2.128 μm can be converted to the followed form at λ_ω = 10.6 μm.

$$d_{\text{in}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0.26 & 27.6 \\ 27.6 & -11.8 & 19.3 & 0.6 & 0 & 0 \\ 0.26 & 0.6 & 0 & 19.3 & 0 & 0 \end{bmatrix} \tag{S20}$$

Referencing the SHG PM angles of 10.6 μm and the [d_{in}] matrix (S20), the spatial distribution of d_{eff} can be determined by the Eq. (S12). In the (128°, 0°), (130.1°, 17.3°), and (36.6°, 50.3°) directions, the calculated d_{eff} values are 22.6, 14.0, and 13.2 pm/V, respectively, which are basically consistent with above experimental values. This experiment further proves the reliability of the matrix (S18).

At the end of this part, we introduce some other experimental results that can extra confirm the new calibrated $|d_{eff}|$ values of BGSe crystal. With the tuning femtosecond laser (ORPHEUS-HP, Light Conversion Inc.) as the fundamental light source, under weak focusing ($L < L_R$, where L_R is Rayleigh length) and nonstationary ($L >> L_{nst}$) conditions, the SHG experiments of 1550 nm were performed by GdCOB ($GdCa_4O(BO_3)_3$) and YCOB ($YCa_4O(BO_3)_3$) crystals respectively. The GdCOB was cut along (146.4°, 0°) whose d_{eff} was 1.10 pm/V, and the YCOB was cut along (139.7°, 0°) whose d_{eff} was 1.23 pm/V. Both crystals are 10 mm in length. In small signal output region, when the SHG power was 0.5-3 mW, the fundamental power was

12-24 mW for the (146.4°, 0°)-cut GdCOB, and 11-23 mW for the (139.7°, 0°)-cut YCOB. Assuming these two crystals are reference samples, taking their parameters and experimental results into the Eq. (S13), the $|d_{\text{eff}}|$ of the (116.9°, 0°)-cut BGSe in Fig. S1 will be calibrated as 21±2, 23±3 pm/V respectively. These data basically agree with the value of 24.3 pm/V when the LBO crystal was used as reference sample. The SHG experimental results of GdCOB, YCOB crystals reconfirm that our calibrations about BGSe crystal are reliable.

4. Other measurements

(1) Transmission spectrum

We used the 2.5 mm thick, (63.1°, 0°) BGSe sample to measure the transmittance in the range of 0-25 μm. As shown in Fig. S2, the BGSe sample exhibited a wide transmission range from 0.47 to 18.9 μm, in which no absorption peak is observed. When the wavelength is 10 μm, the transmittance is 68%. According to the refractive index of BGSe crystal [3], the surface reflectivity of single end face is 17% at 10 μm, and the total reflective loss of the two end faces will be ~34%. So the absorption loss in the crystal sample can be seemed as zero. In short, the transmission spectrum shows that our BGSe crystal has high optical quality.

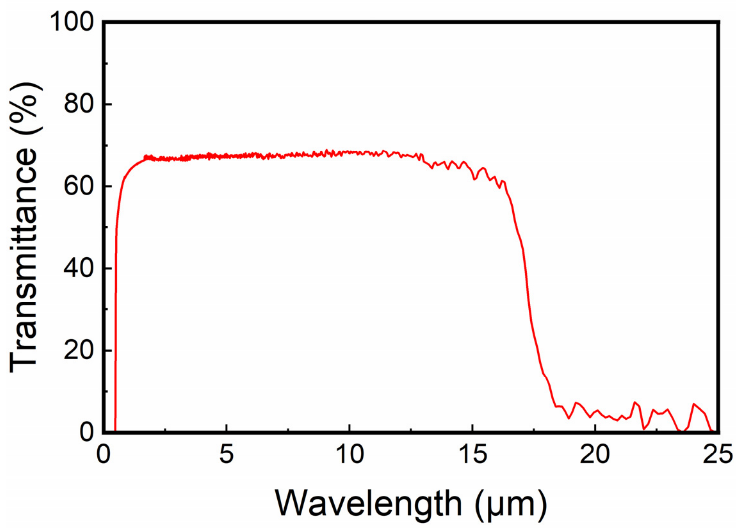

Fig. S2. Transmission spectrum of the 2.5 mm thick, (63.1°, 0°) BGSe sample.

(2) Laser damage threshold

The laser damage threshold of BGSe crystal was measured with the pulsed CO_2 laser. The original laser beam was approximate Gaussian distribution. It was focused by a convex lens whose focal length was 500 mm. The 2.5 mm thick, (63.1°, 0°) BGSe sample was placed before the focus about 100 mm. The beam diameter was measured by the knife-edge method, which was determined by the position difference at where the ratios of the transmitted light intensity to the total incident light intensity are 13.5% ($1/e^2$), 86.5% ($1-1/e^2$), respectively. Under 10.6 μm, 100 ns, 1 Hz laser pulse conditions, the damage threshold of BGSe crystal was measured to be 366 MW/cm^2.

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