Supporting Information

Ba₆In₆Zn₄Se₁₉: A High Performance Infrared Nonlinear Optical Crystal with [InSe₃]³⁻ Trigonal Planar Functional Motifs

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Raman Measurements

The Raman spectrum was collected with powder of Se19 on a Labram HR800 Evolution spectrometer equipped with a CCD detector using 532 nm radiations from a diode laser. Powder were loaded on a clean glass slide. The measurement range is 100-4000cm⁻¹. The laser spot diameter is less than 1µm, and test time is less than 60s.

Based on the Raman spectra, it can be separated to two ranges of vibrations among them, *i.e.* the low-frequency modes (above 200cm⁻¹) are highly covalent whereas the high-frequency modes are mainly ionic (below 200 cm⁻¹). They are related to In\Zn-Se and Ba-Se vibrations, respectively. The vibration of covalent bonds is more important for nonlinear optics, so we focus on the vibration of covalent bonds. The vibrations of covalent bonds in Se19 located at 210 to 250 cm⁻¹ with a dominating line at 240 cm⁻¹.

Computational Details and Formula for SHG Calculations

Due to a co-occupied position of In and Zn in the structure, tens thousands of models (combination: 12870) of Se19 are built under the chemical composition ratio. These structures are optimized, and the model with the lowest energy (Figure S14) is selected for optical properties calculation.

The calculations of optical properties in terms of the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is given by

$$\varepsilon_{2}^{ij}(\omega) = \frac{8\pi^{2}h^{2}e^{2}}{m^{2}V_{eff}} \Sigma_{k} \Sigma_{cv} (f_{c} - f_{v}) \frac{p_{cv}^{i}(k)p_{vc}^{j}(k)}{E_{vc}^{2}} \delta[E_{cv}(k) - h\omega]$$
(S1)

where $\delta[E_{cv}(k) - \hbar\omega]$ denotes the energy difference between the conduction and valence bands at the *k* point with absorption of a quantum $\hbar\omega$. The f_c and f_v represent the Fermi distribution functions of the conduction and valence bands, respectively. The term $p_{cv}^i(k)$ denotes the momentum matrix element transition from the energy level *c* of the conduction band to the level *v* of the valence band at the *k* point in the Brillouin zones and *V* is the volume of the unit cell. The *m*, *e* and \hbar are the electron mass, charge and Plank's constant, respectively. The real part $\varepsilon_1(\omega)$ is given through the Kramer–Kroning transformation.

Then, the refractive index is given by:

$$n(\omega) = \sqrt{\frac{\varepsilon_1(\omega) + \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}{2}}$$
(S2)

The SHG coefficient is based on the susceptibility formula by the perturbation method of Sipe, and the definition of δ function to obtain susceptibility formula as follows.

For the V-C process (electronic transition from valence to conduction bands):

$$\chi_{abc}^{(2,l)}(-2\omega;\omega,\omega) = \frac{-e^{3}h^{3}}{m^{3}\Omega} \sum_{ijlK}^{i\in V, j\in C, j\neq l} \frac{3\eta}{|0.5E_{ji}(K) - E_{li}(K)|} \left[\frac{\delta(E - 0.5E_{ji}(K))}{0.25E_{ji}^{4}(K)} + \frac{\delta(E - E_{li}(K))}{4E_{li}^{4}(K)}\right] P_{abc}(p_{ij}^{a}(K)p_{jl}^{b}(K)p_{li}^{c}(K))$$
(S3)

For V-V and V-C mixing processes :

$$\chi_{abc}^{(2,II)}(-2\omega;\omega,\omega) = \frac{e^{3}\mathbf{h}^{3}}{m^{3}\Omega} \sum_{ijlK}^{ileV,j\in C,i\neq l} \frac{3\eta}{|0.5E_{ji}(K) - E_{jl}(K)|} \left[\frac{\delta(E-0.5E_{ji}(K))}{0.25E_{ji}^{4}(K)} + \frac{\delta(E-E_{jl})}{4E_{jl}^{4}(K)}\right] P_{abc}(p_{ll}^{a}(K)p_{jj}^{b}(K)p_{jl}^{c}(K))$$
(S4)

Where,
$$P_{abc}(p_{li}^{a}(K)p_{ij}^{b}(K)p_{jl}^{c}(K)) = 0.5P_{bc}(p_{li}^{a}(K)p_{ij}^{b}(K)p_{jl}^{c}(K) + p_{ij}^{a}(K)p_{jl}^{b}(K)p_{lj}^{c}(K) + p_{ij}^{a}(K)p_{li}^{b}(K)p_{li}^{c}(K))$$

In the formulas (S3) and (S4), the $\delta(x)$ is a δ function and η is damping factor (0.15 is adopted in this work). The moment matrix elements $p_{ij}(K)$ and energy $E_{ij}(K)$ were obtained from the DFT calculations embedded in CASTEP code. In the DFT calculations, we can obtain the imaginary part of $\chi_{abc}^{(2)} = \chi_{abc}^{(2,I)} + \chi_{abc}^{(2,II)}$ by using formulas (S3) and (S4). The real part $\chi^{(2)}$ is obtained by Kramers-Kronig transform from the imaginary part $\chi^{(2)}$. Here note that $\chi^{(2)} = [(r\chi^{(2)})^2 + |(i\chi^{(2)})^2|]^{1/2}$, and the NLO parameter $2d = \chi^{(2)}$.

From the summation equation S3 and S4, we can decompose the NLO coefficient onto a specific valance band *i* as following:

$$\begin{split} \chi_{abc}(-2\omega;\omega,\omega) &= \frac{-e^{3}h^{3}}{m^{3}\Omega} \sum_{i}^{5} \left(\sum_{jlK}^{jl\in C, j\neq l} \frac{3\eta}{|0.5E_{ji}(K) - E_{li}(K)|} \left[\frac{\delta(E - 0.5E_{ji}(K))}{0.25E_{ji}^{4}(K)} + \frac{\delta(E - E_{li}(K))}{4E_{li}^{4}(K)}\right] + \sum_{jlK}^{leV, j\in C, i\neq l} \left[\frac{3\eta}{|0.5E_{ji}(K) - E_{jl}(K)|} \left[\frac{\delta(E - 0.5E_{ji}(K))}{0.25E_{ji}^{4}(K)} + \frac{\delta(E - E_{jl})}{4E_{li}^{4}(K)}\right]\right] + \sum_{jlK}^{leV, j\in C, i\neq l} \left[\frac{3\eta}{|0.5E_{ji}(K) - E_{jl}(K)|} \left[\frac{\delta(E - 0.5E_{ji}(K))}{0.25E_{ji}^{4}(K)} + \frac{\delta(E - E_{jl})}{4E_{jl}^{4}(K)}\right]\right]\right] + \sum_{jlK}^{leV, j\in C, i\neq l} \left[\frac{3\eta}{|0.5E_{ji}(K) - E_{jl}(K)|} \right] \left[\frac{\delta(E - 0.5E_{ji}(K))}{0.25E_{ji}^{4}(K)} + \frac{\delta(E - E_{jl})}{4E_{jl}^{4}(K)}\right]\right] + \sum_{jlK}^{leV, j\in C, i\neq l} \left[\frac{3\eta}{|0.5E_{ji}(K) - E_{jl}(K)|} \right] \left[\frac{\delta(E - 0.5E_{ji}(K))}{0.25E_{ji}^{4}(K)} + \frac{\delta(E - E_{jl})}{4E_{jl}^{4}(K)}\right] \left[\frac{\delta(E - 0.5E_{ji}(K))}{4E_{jl}^{4}(K)} + \frac{\delta(E - E_{jl})}{4E_{jl}^{4}(K)}\right]\right] + \sum_{jlK}^{leV, j\in C, i\neq l} \left[\frac{\delta(E - 0.5E_{ji}(K))}{0.25E_{ji}^{4}(K)} + \frac{\delta(E - E_{jl})}{16E_{jl}^{4}(K)}\right] \left[\frac{\delta(E - 0.5E_{ji}(K))}{16E_{jl}^{4}(K)} + \frac{\delta(E - E_{jl})}{16E_{jl}^{4}(K)}\right] \left[\frac{\delta(E - 0.5E_{ji}(K))}{16E_{jl}^{4}(K)} + \frac{\delta(E - 0.5E_{ji}(K))}{16E_{jl}^{4}(K)} + \frac{\delta(E - 0.5E_{ji}(K))}{16E_{jl}^{4}(K)}\right] \left[\frac{\delta(E - 0.5E_{ji}(K))}{16E_{jl}^{4}(K)} + \frac{\delta(E - 0.5E_{ji}(K))}{16E_{jl}^{4}(K)} + \frac{\delta(E - 0.5E_{ji}(K))}{16E_{jl}^{4}(K)} + \frac{\delta(E - 0.5E_{ji}(K)}{16E_{jl}^{4}(K)} + \frac{\delta(E - 0.5E_{ji}(K))}{16E_{jl}^{4}(K)} + \frac{\delta(E - 0.5E_{ji}(K))}{16E_{jl}^{4}(K)} + \frac{\delta(E - 0.5E_{ji}(K)}{16E_{jl}^{4}(K)} + \frac{\delta(E - 0.5E_{ji}(K)}{16E_{ji}^{4}(K)} + \frac{\delta(E - 0.5E_{ji}(K)}{16E_{j$$

By summation all the valence band, the total χ_{abc} was evaluated and the contribution of each valance band is straightforward to calculate. We further use the Bader charge analysis to decompose every valance band to the component atoms, so the percentage of each component atom in the valance band is obtained and also the atomic contribution to the SHG coefficient and birefringence can be obtained by summation of all valence bands.

FIGURES and TABLES

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Figure S5. SHG signals of of Se19-1, Se19-2, Se19-3 and AGS at 150-210µm.

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Figure S6. TGA curves for Se19-1, Se19-2 and Se19-3.

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Table S1 Crystal data and structure refinement for Se19.

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 Table S4. LIDT measurement results

Element Analysis

A field emission scanning electron microscope (SEM, FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDX, Oxford INCA) is used for collecting EDX data for Se19 (**Figure S1**). Electron Backscattered Diffraction (EBSD) on clean crystal surfaces of Se19-1, Se19-2, Se19-3, Se19 composite were also observed (**Figure S5**).



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Formula	$\mathrm{Ba}_{6}\mathrm{In}_{6}\mathrm{Zn}_{4}\mathrm{Se}_{19}$
Formula weight	3274.68
Wavelength	0.71073 Å
Temperature	293(2) K

Table S1. Crystal data and structure refinement for Se19.

Crystal system	Tetragonal	
Space group	P-42 ₁ m(113)	
Unit cell dimensions	a = b = 17.3486(4) Å	
	c = 6.7184(8) Å	
	$\alpha = \beta = \gamma = 90^{\circ}C$	
Volume	2022.1(3) Å ³	
Z, Calculated density	2, 5.378 g·cm ⁻³	
Absorption coefficient	28.507 mm ⁻¹	
F(000)	2792	
Theta range	2.63° to 27.49°	
Refinement method	Full-matrix least-squares on F ²	
Completeness	99.9 %	
Absorption correction	Multi-scan	
Goodness-of-fit on F ²	1.153	
Final R indices	R1=0.0275, wR2=0.0502	
R indices (all data)	R1=0.0272, wR2=0.0505	
peak and hole	1.6 and -0.9 e.Å ⁻³	

Table S2.	Selected bond	l lengths (Å) of Ba ₆ In ₆ Zn	4Se19.
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Atom1	Atom2	Count	Bond length
Ba1	Se5	1x	3.2622(13)
	Se2	1x	3.2805(13)
	Se6	1x	3.2987(13)
	Se6	1x	3.4481(13)
	Se5	1 x	3.4507(13)

	Se4	1x	3.5022(14)
	Se4	1x	3.5149(14)
	Se7	1 x	3.5486(13)
Ba2	Se3	1 x	3.2589(15)
	Se4	2x	3.2592(13)
	Se7	1 x	3.3488(17)
	Se1	1x	3.3586(7)
	Se6	2x	3.4903(13)
	Se7	1x	3.6167(17)
In1	Se7	2x	2.5238(89)
	Se1	1x	2.7472(337)
Inla	Se7	2x	2.5705(508)
	Se1	1x	2.7152(341)
	Se2	1x	2.7340(513)
In2	Se5	4x	2.5848(11)
In3 Zn3	Se6	1x	2.4848(15)
	Se5	1x	2.4932(14)
	Se4	1x	2.5256(14)
	Se3	1x	2.5704(15)
In4 Zn4	Se4	2x	2.5224(14)
	Se2	1x	2.5638(24)
	Se1	1x	2.6476(12)

(i) x, y, 1+z; (ii) -1-y, x, -z; (iii) y, -1-x, 1-z; (iv) -1-y, x, 1-z; (v) 0.5+x, -0.5-y, -z; (vi) y, -1-x, -z; (vii) -0.5-y, -0.5-x, 1+z; (viii) -0.5-y, -0.5-x, z; (ix) 0.5+x, -0.5-y, 1-z; (x) -1-x, -y, z; (xi) -1-x, -y, z; (xi) -1-x, -y, z;

Atom1	Atom2	Atom2	Angle 2,1,3
Inl	Se7	Se7	149.439(34)
	Se7	Se1	105.28(3)
	Se7	Se1	105.28(3)
Inla	Se7	Se7	142.561(2198)
	Se7	Se1	104.905(1294)
	Se7	Se2	94.909(1658)
	Se7	Se1	104.906(1294)
	Se7	Se2	94.909(1658)
	Sel	Se2	111.263(1364)
In2	Se5	Se5	115.554(33)
	Se5	Se5	97.890(33)
	Se5	Se5	115.554(33)
	Se5	Se5	115.554(33)
	Se5	Se5	97.890(33)
	Se5	Se5	115.554(33)
In3 Zn3	Se6	Se5	117.419(52)
	Se6	Se4	109.958(49)
	Se6	Se3	105.542(52)
	Se5	Se4	101.148(46)
	Se5	Se3	111.949(49)
	Se4	Se3	110.855(49)
In4 Zn4	Se4	Se4	133.215(49)
	Se4	Se2	105.039(55)
	Se4	Se1	96.242(37)
	Se4	Se2	105.039(55)
	Se4	Sel	96.242(37)
	Se2	Sel	123.295(50)

Table S3. Selected bond angles of $Ba_6In_6Zn_4Se_{19}$.

Comp.	Energy/mJ	Laser spot area/cm ²	LIDT
			MW/cm ²
AGS (150-210 μm)	1.1	0.04909	2.2409
ZnSe (150-210 μm)	22	0.04909	44.8180
Se19-3 (150-210 µm)	19	0.04909	38.7065
Se19-2 (150-210 µm)	17	0.04909	34.6321
Se19-1 (150-210 µm)	6	0.04909	12.2231

 Table S4. LIDT measurement results.