Supplementary Materials

for

Wide band gap selenide infrared nonlinear optical materials $A^{II}Mg_6Ga_6Se_{16}$ with strong SHG responses and high laser-induced damage thresholds

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EXPERIMENTS AND CALCULATIONS

1 Reagents. Mg (99 %), Ca (99.5 %), Sr (99.9 %), Ba (99.9 %), Ga (99.999 %) and Se (99.9 %) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (China). The raw reagents were stored in a dry Ar-filled glove box with oxygen and moisture levels below 0.1 ppm, and utilized without further purifications.

2 Syntheses. The crystallized samples of the title compounds were fabricated by the high temperature solid-state reactions with the starting mixtures Ca/Sr/Ba : Mg : Ga : Se = 1 : 6 : 6 : 16. First, the mixtures were mixed, ground and put into graphite crucibles. Then, the crucibles were placed into quartz tubes, which were further sealed with oxyhydrogen flame under a high vacuum of 10^{-3} Pa. After that, the samples were put into a computer-controlled furnace and slowly heated to 900 °C, kept for 2000 mins, then cooled to room temperature in 8600 mins. After reactions, the pure polycrystalline powder samples were harvested.

3 Single-Crystal X-ray Diffractions. A Bruker SMART APEX II CCD single crystal X-ray diffractometer using Mo Kα radiation (λ = 0.71073 Å) was performed to measure crystal diffraction data at room temperature. The SAINT program was utilized to integrate the diffraction data.[1] The crystal structures were refined and resolved by the SHELXTL program package.[2]

4 Energy-Dispersive X-ray Spectroscopy (EDS). The EDS spectra of the single crystals were characterized on a field emission scanning electron microscope (FE-SEM, JEOL JSM-7610F Plus, Japan) equipped with an energy-dispersive X-ray spectrometer (Oxford, X-Max 50).

5 Raman Spectroscopy. The powder samples were placed on the glass plates and tested by a LABRAM HR Evolution spectrometer (Japan) equipped with a CCD detector (532 nm radiation). The spectra were collected from 4000 to 40 cm^{-1}.

6 Powder X-ray Diffractions. A Bruker D2 PHASER diffractometer (Germany) with Cu Kα radiation (λ = 1.5418 Å) was applied for the measurement of powder XRD patterns at room temperature. The 2θ range was set to 5−70 ° with a fixed counting time of 1 s/step.

7 UV-Vis-NIR Diffuse Reflectance Spectroscopy. The optical diffuse-reflectance spectra of powder samples were tested on a SolidSpec-3700DUV spectrophotometer from 176 to 2600 nm at room temperature. The collected spectra data were converted to optical absorbance by the Kubelka-Munk function:[3]

$$F(R) = K/S = (1-R)^2/2R \quad (1)$$

where, R, K and S represent the reflection coefficient, absorption value, scattering coefficient, respectively.

8 LIDT Measurements. The LIDTs of powder samples with the particle size of ≤ 45 μm were evaluated by the single-pulse LIDT method with an incident laser at 1.06 μm (frequency f = 10 Hz and pulse width τ_p = 10 ns) at room temperature, where AGS samples with same size were used as the references.[4]

9 SHG Measurements. The SHG responses of powder samples were evaluated by the Kurtz-Perry method.[5] The polycrystalline samples of the title compounds were ground and sieved into distinct particle size ranges (≤ 45, 45−63, 63−90, 90−125, 125−180 and 180−212 μm), and AGS powder samples with same particle sizes were

used as the references. The measurements were carried out on a 2.09-μm Q-switch laser at room temperature.

10 Theoretical Calculations. The band structures, partial and total density of states and birefringences of $A^{II}Mg_6Ga_6Se_{16}$ (A^{II} = Ca, Sr, Ba) were calculated by the plane wave pseudopotential method that implemented in the CASTEP software.[6] The exchange-correlation potential was treated by the Perdew-Burke-Ernzerhof (PBE) method in the generalized gradient approximation (GGA).[7] The interactions between the ionic cores and electrons were described by norm-conserving pseudopotential (NCP).[8] The following orbital electrons were treated as valence electrons: Ca $3s^23p^64s^2$, Sr $4s^24p^65s^2$, Ba $6s^25p^66s^2$, Mg $2s^22p^63s^2$, Ga $3d^{10}4s^24p^1$ and Se $4s^24p^4$ in the calculations. The plane-wave energy cutoff was set to 900 eV, and Monkhorst-Pack k-point meshes were adopted by 3 × 3 × 6 with a density < 0.02 $Å^{-1}$ in the Brillouin zone (BZ).[9] The Heyd-Scuseria-Ernzerhof 06 (HSE06) hybrid function was performed using the PWmat code, which runs on graphics processing unit processors (GPU).[10] The other calculation parameters and convergent criteria used the default values of the CASTEP code.

The static SHG susceptibilities can be ascribed to virtual electron (VE) and virtual-hole (VH) processes. At a zero frequency, the formula of second-order NLO coefficients can be derived as:[11]

$$\chi^{(2)}_{\alpha\beta\gamma} = \chi^{(2)}_{\alpha\beta\gamma}(VE) + \chi^{(2)}_{\alpha\beta\gamma}(VH) \tag{2}$$

$$\chi^{(2)}_{\alpha\beta\gamma}(VE) = \frac{e^3}{2\hbar^2 m^3}\sum_{vv'c}\int\frac{d^3k}{4\pi^3}P(\alpha\beta\gamma)Im[P^{\alpha}_{vv'}P^{\beta}_{cv}P^{\gamma}_{cv}]\left(\frac{1}{\omega^3_{cv}\omega^2_{v'c}}+\frac{1}{\omega^4_{vc}\omega_{cv'}}\right) \tag{3}$$

$$\chi^{(2)}_{\alpha\beta\gamma}(VH) = \frac{e^3}{2\hbar^2 m^3}\sum_{vcc'}\int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) Im[P^{\alpha}_{cv} P^{\beta}_{cc'} P^{\gamma}_{c'v}]\left(\frac{1}{\omega^3_{cv}\omega^2_{vc'}} + \frac{1}{\omega^4_{vc}\omega_{c'v}}\right) \quad (4)$$

where, α, β and γ are the Cartesian components; v and v' are the denote valence bands; c and c' are the denote conduction bands; $P(\alpha\beta\gamma)$ is full permutation; $\hbar\omega_{ij}$ is the band energy difference; P_{ij} is the momentum matrix elements.

The hyperpolarizabilities (β) were computed by Gaussian 09 revision D.01 program.[10] The GaussView 5 software visualizes the output file.β_i and β_{tot} can be expressed as:

$$\beta_i = \frac{1}{3}\sum_j \beta_{ijj} + \beta_{jji} + \beta_{jjj},\ i,j = \{x, y, z\} \quad (5)$$

$$\beta_{tot} = \sqrt{(\beta_x^2 + \beta_y^2 + \beta_z^2)} \quad (6)$$

Response Electron Distribution Anisotropy Index (REDA, ζ) reflects birefringence and response charge density can be reduced by:[12]

$$\zeta = \sum_g \left[\frac{N_c Z_a \Delta\rho^b}{n_1 E_o}\right]_g \quad (7)$$

where N_c represents nearest neighbor coordination number, Z_a is formal charge of anion; $\Delta\rho^b = \rho^b_{max} - \rho^b_{min}$, ρ^b_{max} and ρ^b_{min} are the maximum and minimum of the covalent electron density of the covalent bond on the optical principal axes of a crystal; n_1 and E_o are the minimum refractive index and optical band gap, respectively.

Table S1. Crystal data and structure refinements for $A^{II}Mg_6Ga_6Se_{16}$ (A^{II} = Ca, Sr, Ba).

Empirical formula	$CaMg_6Ga_6Se_{16}$	$SrMg_6Ga_6Se_{16}$	$BaMg_6Ga_6Se_{16}$
Formula weight	1867.62	1915.16	1964.88
Crystal system	hexagonal		
Space group	$P\bar{6}$		
a/Å	17.5327(3)	17.6115(9)	17.7326(6)
c/Å	7.7603(2)	7.7684(3)	7.7899(3)
Volume/Å^3	2065.89(9)	2086.70(2)	2121.33(17)
Z	3	3	3
ρ_{calc}/g cm^{-3}	4.504	4.572	4.614
μ/mm^{-1}	27.248	28.689	27.719
F(000)	2466.0	2520.0	2574.0
2θ range for data collection/°	4.646 to 72.664	4.626 to 54.932	4.594 to 54.96
Index ranges	$-29 \le h \le 29$, $-29 \le k \le 29$, $-12 \le l \le 12$	$-22 \le h \le 22$, $-22 \le k \le 22$, $-10 \le l \le 10$	$-22 \le h \le 23$, $-23 \le k \le 23$, $-10 \le l \le 10$
Independent reflections	7002 [R_{int} = 0.0884, R_{sigma} = 0.0534]	3406 [R_{int} = 0.0605, R_{sigma} = 0.0399]	3453 [R_{int} = 0.0575, R_{sigma} = 0.0385]
Data/restraints/parameters	7002/0/153	3406/0/152	3453/0/154
Goodness-of-fit on F^2	1.081	1.023	1.022
R_1, wR_2 [$I > 2\sigma(I)$] [a)]	0.0389, 0.0989	0.0243, 0.0574	0.0261, 0.0618
R_1, wR_2 [all data] [a)]	0.0537, 0.1089	0.0394, 0.0647	0.0338, 0.0670
Largest diff. peak/hole/e Å^{-3}	1.84/-1.74	1.51/-0.88	1.73/-1.32
Flack parameter	0.028(9)	-0.013(14)	0.018(12)

[a)] $R_1 = F_o - F_c/F_o$ and $wR_2 = [w(F_o^2 - F_c^2)^2/wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence calculations for $CaMg_6Ga_6Se_{16}$.

Atom	Wyckoff	*x*	*y*	*z*	U(eq)	BVS[a)]
Ca1	1*e*	6666.67	3333.33	10000	14.2(10)	1.64
Ca2	1*a*	10000	10000	10000	15.1(12)	1.62
Ca3	1*c*	3333.33	6666.67	10000	25.7(16)	1.63
Mg1	3*k*	10436(4)	8017(3)	5000	7.2(9)	1.95
Mg2	3*j*	7494(4)	9485(4)	10000	9.3(10)	2.05
Mg3	3*k*	3803(4)	4728(4)	5000	10.5(10)	1.90
Mg4	3*j*	3873(4)	4732(4)	10000	9.2(9)	1.90
Mg5	3*k*	4300(4)	1342(4)	5000	9.1(9)	2.07
Mg6	3*j*	4200(5)	1340(5)	10000	14.8(11)	2.10
Ga1	6*l*	8128.8(8)	7804.2(8)	7484.4(14)	7.2(2)	2.95
Ga2	6*l*	5592.1(8)	7020.2(8)	7493.0(14)	6.8(2)	3.06
Ga3	6*l*	4705.4(8)	3572.1(7)	7493.5(16)	6.5(2)	3.00
Se1	6*l*	8421.2(8)	9264.6(7)	7545.6(16)	9.7(2)	1.93
Se2	3*j*	5893.2(12)	7952.6(13)	10000	8.1(3)	2.02
Se3	3*j*	8726.9(13)	7431.8(11)	10000	8.0(3)	1.88
Se4	3*k*	8670.5(13)	7360.3(11)	5000	7.1(3)	1.93
Se5	6*l*	6657.5(7)	6541.9(7)	7506.5(19)	6.44(18)	2.19
Se6	6*l*	4111.0(8)	5875.0(9)	7524.3(14)	9.38(18)	1.92
Se7	3*k*	2008.7(15)	4038.3(12)	5000	8.3(3)	2.02
Se8	6*l*	3249.0(7)	3368.0(8)	7507.1(18)	6.45(19)	1.86
Se9	3*k*	5281.3(11)	4551.9(11)	5000	7.2(3)	2.00
Se10	3*j*	5335.4(12)	4543.2(11)	10000	7.4(3)	1.90
Se11	6*l*	5093.8(9)	2473.6(8)	7536(2)	8.63(18)	2.00
GII[b)]				0.155		

[a)]The bond valence sum is calculated by bond-valence theory ($S_{ij} = \exp[(R_0\text{-}R)/B$, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and B= 0.37).

[b)]The global instability index (GII) calculated using

$$G = \sqrt{\frac{\sum_{i=1}^{n} (BVS - v_i)}{N}}$$

where N is the number of atoms in the formula unit. The GII is calculated as 0.155 which is lower than 0.2 indicating the rationality of the structure from this side.

Table S3 Selected bond lengths [Å] for $CaMg_6Ga_6Se_{16}$.

Atom	Atom	Length	Atom	Atom	Length
Ca1	Se11[1]	3.0612(15)	Mg3	Se8[16]	2.844(5)
Ca1	Se11	3.0612(15)	Mg3	Se8	2.844(5)
Ca1	Se11[5]	3.0612(15)	Mg3	Se9	2.762(8)
Ca1	Se11[3]	3.0612(15)	Mg4	Se2[11]	2.798(7)
Ca1	Se11[4]	3.0612(15)	Mg4	Se6	2.652(4)
Ca1	Se11[2]	3.0612(15)	Mg4	Se6[1]	2.652(4)
Ca2	Se1[6]	3.0640(13)	Mg4	Se8[1]	2.836(4)
Ca2	Se1[8]	3.0640(13)	Mg4	Se8	2.836(4)
Ca2	Se1[9]	3.0640(12)	Mg4	Se10	2.747(8)
Ca2	Se1[7]	3.0640(12)	Mg5	Se4[3]	2.883(6)
Ca2	Se1[1]	3.0640(13)	Mg5	Se5[17]	2.727(5)
Ca2	Se1	3.0640(12)	Mg5	Se5[3]	2.727(5)
Ca3	Se6[10]	3.0609(12)	Mg5	Se9[3]	2.717(6)
Ca3	Se6[1]	3.0609(12)	Mg5	Se11[16]	2.640(5)
Ca3	Se6[11]	3.0609(12)	Mg5	Se11	2.640(5)
Ca3	Se6[12]	3.0609(12)	Mg6	Se3[3]	2.820(7)
Ca3	Se6	3.0609(12)	Mg6	Se5[3]	2.691(5)
Ca3	Se6[13]	3.0609(12)	Mg6	Se5[4]	2.691(5)
Mg1	Se1[7]	2.668(4)	Mg6	Se10[3]	2.809(7)
Mg1	Se1[14]	2.668(4)	Mg6	Se11	2.638(5)
Mg1	Se4	2.712(6)	Mg6	Se11[1]	2.638(5)
Mg1	Se7[5]	2.816(7)	Ga1	Se1	2.3476(15)
Mg1	Se8[15]	2.791(4)	Ga1	Se3	2.454(2)
Mg1	Se8[5]	2.791(4)	Ga1	Se4	2.442(2)
Mg2	Se1[1]	2.652(4)	Ga1	Se5	2.4168(15)
Mg2	Se1	2.652(4)	Ga2	Se2	2.4235(19)
Mg2	Se2	2.752(8)	Ga2	Se5	2.3998(15)
Mg2	Se3[6]	2.769(7)	Ga2	Se6	2.3591(15)
Mg2	Se8[12]	2.752(4)	Ga2	Se7[12]	2.420(2)
Mg2	Se8[10]	2.752(4)	Ga3	Se8	2.3942(16)
Mg3	Se6[16]	2.663(5)	Ga3	Se9	2.4448(17)
Mg3	Se6	2.663(5)	Ga3	Se10	2.4550(17)
Mg3	Se7	2.745(7)	Ga3	Se11	2.3417(14)

[1]+X,+Y,2-Z; [2]1+Y-X,1-X,2-Z; [3]1-Y,+X-Y,+Z; [4]1-Y,+X-Y,2-Z; [5]1+Y-X,1-X,+Z; [6]1+Y-X,2-X,+Z; [7]2-Y,1+X-Y,+Z; [8]1+Y-X,2-X,2-Z; [9]2-Y,1+X-Y,2-Z; [10]1-Y,1+X-Y,2-Z; [11]+Y-X,1-X,+Z; [12]1-Y,1+X-Y,+Z; [13]+Y-X,1-X,2-Z; [14]2-Y,1+X-Y,1-Z; [15]1+Y-X,1-X,1-Z; [16]+X,+Y,1-Z; [17]1-Y,+X-Y,1-Z

Table S4. Selected bond angles [°] for $CaMg_6Ga_6Se_{16}$.

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Se11^{2}	Ca1	Se11^{3}	77.29(6)	Se6	Mg3	Se7	95.1(2)
Se11^{2}	Ca1	Se11^{1}	85.13(5)	Se6^{16}	Mg3	Se7	95.1(2)
Se11^{3}	Ca1	Se11^{5}	85.13(5)	Se6	Mg3	Se8^{16}	172.7(3)
Se11^{4}	Ca1	Se11^{5}	77.29(6)	Se6^{16}	Mg3	Se8^{16}	89.12(4)
Se11^{2}	Ca1	Se11^{5}	134.03(2)	Se6	Mg3	Se8	89.12(4)
Se11^{1}	Ca1	Se11	77.29(6)	Se6^{16}	Mg3	Se8	172.7(3)
Se11^{1}	Ca1	Se11^{4}	85.13(5)	Se6	Mg3	Se9	103.59(19)
Se11^{2}	Ca1	Se11^{4}	85.13(4)	Se6^{16}	Mg3	Se9	103.59(19)
Se11^{3}	Ca1	Se11	85.13(5)	Se7	Mg3	Se8	78.30(16)
Se11^{2}	Ca1	Se11	134.03(2)	Se7	Mg3	Se8^{16}	78.30(16)
Se11^{4}	Ca1	Se11	134.03(2)	Se7	Mg3	Se9	152.1(3)
Se11^{3}	Ca1	Se11^{4}	134.03(2)	Se8^{16}	Mg3	Se8	86.37(19)
Se11^{5}	Ca1	Se11	85.13(4)	Se9	Mg3	Se8	81.48(18)
Se11^{1}	Ca1	Se11^{5}	134.03(2)	Se9	Mg3	Se8^{16}	81.48(18)
Se11^{3}	Ca1	Se11^{1}	134.03(2)	Se2^{10}	Mg4	Se8^{1}	77.59(15)
Se1^{9}	Ca2	Se1^{1}	85.41(3)	Se6	Mg4	Se2^{10}	90.89(19)
Se1^{6}	Ca2	Se1	85.41(3)	Se6^{1}	Mg4	Se2^{10}	90.89(19)
Se1^{7}	Ca2	Se1	85.41(3)	Se6^{1}	Mg4	Se6	92.8(2)
Se1^{1}	Ca2	Se1	76.91(5)	Se6^{1}	Mg4	Se8	168.3(3)
Se1^{8}	Ca2	Se1^{9}	85.41(3)	Se6	Mg4	Se8	89.50(5)
Se1^{7}	Ca2	Se1^{9}	76.91(5)	Se6	Mg4	Se8^{1}	168.3(3)
Se1^{9}	Ca2	Se1^{6}	133.897(16)	Se6^{1}	Mg4	Se8^{1}	89.50(5)
Se1^{8}	Ca2	Se1^{6}	76.91(5)	Se6^{1}	Mg4	Se10	106.70(19)
Se1^{1}	Ca2	Se1^{6}	133.897(16)	Se6	Mg4	Se10	106.70(19)
Se1^{8}	Ca2	Se1^{7}	133.897(16)	Se8	Mg4	Se8^{1}	86.01(18)
Se1^{8}	Ca2	Se1	133.898(16)	Se10	Mg4	Se2^{10}	154.1(3)
Se1^{7}	Ca2	Se1^{6}	85.41(3)	Se10	Mg4	Se8	83.55(18)
Se1^{8}	Ca2	Se1^{1}	85.41(3)	Se10	Mg4	Se8^{1}	83.55(18)
Se1^{9}	Ca2	Se1	133.896(16)	Se5^{17}	Mg5	Se4^{3}	80.77(16)
Se1^{7}	Ca2	Se1^{1}	133.897(16)	Se5^{3}	Mg5	Se4^{3}	80.77(16)
Se6^{10}	Ca3	Se6^{11}	134.176(15)	Se5^{17}	Mg5	Se5^{3}	91.0(2)
Se6^{10}	Ca3	Se6^{1}	134.176(15)	Se9^{3}	Mg5	Se4^{3}	158.7(3)
Se6^{11}	Ca3	Se6	134.176(16)	Se9^{3}	Mg5	Se5^{3}	84.35(16)
Se6^{12}	Ca3	Se6	84.80(3)	Se9^{3}	Mg5	Se5^{17}	84.35(16)
Se6^{13}	Ca3	Se6^{1}	84.80(3)	Se11^{16}	Mg5	Se4^{3}	99.41(16)
Se6^{12}	Ca3	Se6^{1}	134.176(16)	Se11	Mg5	Se4^{3}	99.41(16)
Se6^{10}	Ca3	Se6^{12}	84.80(3)	Se11	Mg5	Se5^{17}	177.2(2)
Se6^{10}	Ca3	Se6^{13}	77.73(4)	Se11^{16}	Mg5	Se5^{3}	177.2(2)
Se6^{11}	Ca3	Se6^{12}	77.73(4)	Se11	Mg5	Se5^{3}	86.27(4)
Se6^{11}	Ca3	Se6^{1}	84.80(3)	Se11^{16}	Mg5	Se5^{17}	86.27(4)

Se6[10]	Ca3	Se6	84.80(3)	Se11[16]	Mg5	Se9[3]	94.72(18)
Se6[11]	Ca3	Se6[13]	84.80(3)	Se11	Mg5	Se9[3]	94.72(18)
Se6[13]	Ca3	Se6[12]	134.176(15)	Se11	Mg5	Se11[16]	96.4(2)
Se6[13]	Ca3	Se6	134.176(15)	Se5[2]	Mg6	Se3[3]	84.26(19)
Se6	Ca3	Se6[1]	77.73(4)	Se5[3]	Mg6	Se3[3]	84.26(19)
Se1[7]	Mg1	Se1[14]	95.49(19)	Se5[3]	Mg6	Se5[2]	92.0(2)
Se1[7]	Mg1	Se4	94.16(18)	Se5[2]	Mg6	Se10[3]	82.91(17)
Se1[14]	Mg1	Se4	94.16(18)	Se5[3]	Mg6	Se10[3]	82.91(17)
Se1[7]	Mg1	Se7[5]	100.78(16)	Se10[3]	Mg6	Se3[3]	161.5(3)
Se1[14]	Mg1	Se7[5]	100.78(16)	Se11[1]	Mg6	Se3[3]	103.49(18)
Se1[7]	Mg1	Se8[5]	88.05(4)	Se11	Mg6	Se3[3]	103.49(18)
Se1[14]	Mg1	Se8[15]	88.05(4)	Se11[1]	Mg6	Se5[2]	87.03(5)
Se1[14]	Mg1	Se8[5]	176.43(19)	Se11[1]	Mg6	Se5[3]	172.0(3)
Se1[7]	Mg1	Se8[15]	176.43(19)	Se11	Mg6	Se5[2]	172.0(3)
Se4	Mg1	Se7[5]	157.7(2)	Se11	Mg6	Se5[3]	87.03(5)
Se4	Mg1	Se8[15]	86.07(16)	Se11[1]	Mg6	Se10[3]	89.12(19)
Se4	Mg1	Se8[5]	86.07(16)	Se11	Mg6	Se10[3]	89.12(19)
Se8[15]	Mg1	Se7[5]	78.00(18)	Se11	Mg6	Se11[1]	92.9(3)
Se8[5]	Mg1	Se7[5]	78.00(18)	Se1	Ga1	Se3	112.67(7)
Se8[15]	Mg1	Se8[5]	88.41(17)	Se1	Ga1	Se4	117.12(7)
Se1[1]	Mg2	Se1	91.88(19)	Se1	Ga1	Se5	123.39(6)
Se1[1]	Mg2	Se2	104.92(19)	Se4	Ga1	Se3	104.89(7)
Se1	Mg2	Se2	104.92(19)	Se5	Ga1	Se3	98.79(7)
Se1	Mg2	Se3[6]	89.3(2)	Se5	Ga1	Se4	96.90(7)
Se1[1]	Mg2	Se3[6]	89.3(2)	Se5	Ga2	Se2	106.69(7)
Se1	Mg2	Se8[12]	89.18(4)	Se5	Ga2	Se7[12]	104.90(7)
Se1[1]	Mg2	Se8[11]	89.18(4)	Se6	Ga2	Se2	109.97(7)
Se1	Mg2	Se8[11]	174.7(3)	Se6	Ga2	Se5	114.86(5)
Se1[1]	Mg2	Se8[12]	174.7(3)	Se6	Ga2	Se7[12]	113.31(7)
Se2	Mg2	Se3[6]	159.3(2)	Se7[12]	Ga2	Se2	106.54(6)
Se2	Mg2	Se8[11]	79.79(19)	Se8	Ga3	Se9	98.24(7)
Se2	Mg2	Se8[12]	79.79(19)	Se8	Ga3	Se10	100.19(7)
Se8[11]	Mg2	Se3[6]	85.51(17)	Se9	Ga3	Se10	104.78(6)
Se8[12]	Mg2	Se3[6]	85.51(17)	Se11	Ga3	Se8	127.20(6)
Se8[12]	Mg2	Se8[11]	89.29(18)	Se11	Ga3	Se9	113.67(9)
Se6[16]	Mg3	Se6	94.8(2)	Se11	Ga3	Se10	110.04(8)

[1]+X,+Y,2-Z; [2]1-Y,+X-Y,2-Z; [3]1-Y,+X-Y,+Z; [4]1+Y-X,1-X,2-Z; [5]1+Y-X,1-X,+Z; [6]1+Y-X,2-X,+Z; [7]2-Y,1+X-Y,+Z; [8]1+Y-X,2-X,2-Z; [9]2-Y,1+X-Y,2-Z; [10]+Y-X,1-X,+Z; [11]1-Y,1+X-Y,2-Z; [12]1-Y,1+X-Y,+Z; [13]+Y-X,1-X,2-Z; [14]2-Y,1+X-Y,1-Z; [15]1+Y-X,1-X,1-Z; [16]+X,+Y,1-Z; [17]1-Y,+X-Y,1-Z; [18]+Y-X,1-X,1-Z

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $CaMg_6Ga_6Se_{16}$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	15.9(15)	15.9(15)	11(2)	0	0	7.9(8)
Ca2	17.6(17)	17.6(17)	10(3)	0	0	8.8(9)
Ca3	21(2)	21(2)	35(4)	0	0	10.4(11)
Mg1	8(2)	9(2)	6(2)	0	0	4.6(19)
Mg2	13(2)	15(2)	5(2)	0	0	10(2)
Mg3	14(2)	10(2)	5(2)	0	0	5(2)
Mg4	13(2)	8(2)	4.8(19)	0	0	4.3(19)
Mg5	9(2)	8(2)	9(2)	0	0	4(2)
Mg6	14(3)	12(3)	16(2)	0	0	4(3)
Ga1	9.6(5)	6.7(5)	5.4(4)	-0.5(4)	-0.3(4)	4.2(4)
Ga2	7.1(5)	7.2(4)	6.0(4)	0.5(3)	0.9(4)	3.4(4)
Ga3	7.5(4)	6.1(4)	6.1(4)	-0.2(4)	0.0(4)	3.5(3)
Se1	12.5(5)	7.3(4)	10.2(5)	-1.8(4)	-1.0(4)	5.6(4)
Se2	10.8(8)	5.2(7)	7.3(6)	0	0	3.2(6)
Se3	7.4(7)	11.8(8)	5.7(5)	0	0	5.5(6)
Se4	9.1(7)	8.5(7)	5.6(5)	0	0	5.8(6)
Se5	6.2(4)	5.8(4)	7.8(4)	-0.1(3)	0.1(3)	3.3(3)
Se6	6.9(4)	8.8(4)	10.1(4)	-0.3(5)	0.9(5)	2.2(4)
Se7	11.9(8)	10.5(7)	6.7(6)	0	0	8.6(6)
Se8	5.1(4)	6.2(4)	7.4(4)	0.3(3)	0.4(3)	2.4(3)
Se9	3.7(6)	8.1(7)	6.2(5)	0	0	0.3(5)
Se10	7.9(7)	5.9(6)	5.4(5)	0	0	1.3(5)
Se11	11.6(4)	7.2(4)	8.2(4)	-1.0(4)	-1.8(4)	5.5(4)

Table S6. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence calculations for $SrMg_6Ga_6Se_{16}$.

Atom	Wyckoff	*x*	*y*	*z*	U(eq)	BVS[a)]
Sr1	1*f*	6666.67	3333.33	10000	27.3(12)	1.87
Sr2	1*d*	3333.33	6666.67	10000	26.3(12)	1.86
Sr3	1*b*	0	0	10000	26.9(12)	1.84
Mg1	3*k*	4669(8)	3853(10)	10000	25(3)	1.90
Mg2	3*j*	5844(9)	8617(8)	10000	23(3)	1.97
Mg3	3*k*	5759(10)	8611(8)	5000	24(2)	2.02
Mg4	3*j*	4641(8)	3780(11)	5000	24(3)	2.02
Mg5	3*j*	2506(10)	512(9)	10000	26(3)	2.12
Mg6	3*k*	2415(9)	393(8)	5000	21(2)	2.06
Ga1	6*l*	6977.2(12)	5519.8(12)	7476(5)	19.9(5)	2.95
Ga2	6*l*	5238.0(11)	6310.7(11)	7479(5)	18.9(4)	3.00
Ga3	6*l*	1963.5(12)	2199.8(12)	7477(4)	18.8(4)	3.06
Se1	6*l*	5785.7(11)	4088.4(11)	7512(4)	20.9(4)	2.02
Se2	3*j*	7966(3)	5948(3)	5000	18.9(8)	2.04
Se3	3*k*	7932(3)	5860(3)	10000	20.7(8)	2.19
Se4	3*k*	6773.8(10)	6778.9(10)	7509(5)	18.6(3)	1.94
Se5	6*l*	4637(3)	5361(3)	5000	18.8(9)	2.03
Se6	6*l*	4962.3(12)	7485.3(12)	7504(5)	20.9(3)	1.90
Se7	3*j*	4586(3)	5392(3)	10000	19.5(9)	1.89
Se8	3*j*	3409.7(11)	3451.2(11)	7508(5)	18.4(3)	1.97
Se9	3*k*	1628.4(12)	734.5(11)	7509(5)	20.9(3)	1.84
Se10	6*l*	1320(3)	2510(3)	10000	18.2(8)	2.07
Se11	3*k*	1373(3)	2590(3)	5000	19.2(8)	1.86
GII[b)]				0.096		

[a)]The bond valence sum is calculated by bond-valence theory ($S_{ij} = \exp[(R_0\text{-}R)/B$, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and B= 0.37).

[b)]The global instability index (GII) calculated using

$$G = \sqrt{\frac{\sum_{i=1}^{n} (BVS - v_i)}{N}}$$

where N is the number of atoms in the formula unit. The GII is calculated as 0.096 which is lower than 0.2 indicating the rationality of the structure from this side.

Table S7. Selected bond lengths [Å] for $SrMg_6Ga_6Se_{16}$.

Atom	Atom	Length	Atom	Atom	Length
Sr1	Se1[2]	3.152(3)	Mg3	Se6[5]	2.759(9)
Sr1	Se1[3]	3.152(3)	Mg3	Se6	2.759(9)
Sr1	Se1[4]	3.152(3)	Mg3	Se11	2.792(15)
Sr1	Se1[5]	3.152(3)	Mg4	Se2	2.784(17)
Sr1	Se1[1]	3.152(3)	Mg4	Se5	2.661(9)
Sr1	Se1	3.152(3)	Mg4	Se5[14]	2.661(9)
Sr2	Se10[7]	3.152(3)	Mg4	Se6[14]	2.752(9)
Sr2	Se10[8]	3.152(3)	Mg4	Se6	2.752(9)
Sr2	Se10[9]	3.152(3)	Mg4	Se7	2.739(16)
Sr2	Se10	3.152(3)	Mg5	Se3[16]	2.702(11)
Sr2	Se10[5]	3.152(3)	Mg5	Se3[11]	2.702(11)
Sr2	Se10[6]	3.152(3)	Mg5	Se7	2.877(14)
Sr3	Se5[5]	3.159(2)	Mg5	Se8[7]	2.748(13)
Sr3	Se5[12]	3.159(2)	Mg5	Se10	2.630(11)
Sr3	Se5[11]	3.159(2)	Mg5	Se10[14]	2.630(11)
Sr3	Se5[10]	3.159(2)	Mg6	Se3[13]	2.702(11)
Sr3	Se5[13]	3.159(2)	Mg6	Se3[11]	2.702(11)
Sr3	Se5	3.159(2)	Mg6	Se9[7]	2.883(15)
Mg1	Se1[5]	2.654(9)	Mg6	Se10	2.627(11)
Mg1	Se1	2.654(9)	Mg6	Se10[5]	2.627(11)
Mg1	Se4[1]	2.827(15)	Mg6	Se11	2.814(16)
Mg1	Se6[1]	2.819(10)	Ga1	Se3	2.419(2)
Mg1	Se6[4]	2.819(10)	Ga1	Se5	2.340(2)
Mg1	Se9[1]	2.744(16)	Ga1	Se7[10]	2.447(5)
Mg2	Se1	2.628(9)	Ga1	Se11[10]	2.454(5)
Mg2	Se1[14]	2.628(9)	Ga2	Se6	2.394(3)
Mg2	Se2[1]	2.754(16)	Ga2	Se8	2.444(4)
Mg2	Se6[15]	2.839(10)	Ga2	Se9	2.459(4)
Mg2	Se6[1]	2.839(10)	Ga2	Se10	2.342(2)
Mg2	Se8[1]	2.767(17)	Ga3	Se1	2.350(2)
Mg3	Se4	2.787(15)	Ga3	Se2	2.420(4)
Mg3	Se5[5]	2.637(9)	Ga3	Se3	2.403(2)
Mg3	Se5	2.637(9)	Ga3	Se4	2.431(4)

[1]1-Y,+X-Y,+Z; [2]1+Y-X,1-X,+Z; [3]1+Y-X,1-X,1-Z; [4]1-Y,+X-Y,1-Z; [5]+X,+Y,1-Z; [6]1-Y,1+X-Y,+Z; [7]+Y-X,1-X,+Z; [8]1-Y,1+X-Y,1-Z; [9]+Y-X,1-X,1-Z; [10]+Y-X,-X,+Z; [11]-Y,+X-Y,+Z; [12]+Y-X,-X,1-Z; [13]-Y,+X-Y,1-Z; [14]+X,+Y,-Z; [15]1-Y,+X-Y,-Z; [16]-Y,+X-Y,-Z

Table S8. Selected bond angles [°] for $SrMg_6Ga_6Se_{16}$.

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
$Se1^{2}$	Sr1	$Se1^{3}$	133.56(4)	Se5	Mg3	Se4	104.2(4)
$Se1^{2}$	Sr1	$Se1^{1}$	86.13(9)	$Se5^{4}$	Mg3	Se5	94.3(4)
Se1	Sr1	$Se1^{2}$	86.13(9)	Se5	Mg3	$Se6^{4}$	174.7(6)
$Se1^{4}$	Sr1	$Se1^{2}$	133.56(4)	Se5	Mg3	Se6	88.08(9)
$Se1^{3}$	Sr1	$Se1^{1}$	75.92(12)	$Se5^{4}$	Mg3	$Se6^{4}$	88.08(9)
Se1	Sr1	$Se1^{4}$	75.91(12)	$Se5^{4}$	Mg3	Se6	174.7(6)
Se1	Sr1	$Se1^{3}$	133.56(4)	$Se5^{4}$	Mg3	Se11	88.9(4)
Se1	Sr1	$Se1^{1}$	86.13(9)	Se5	Mg3	Se11	88.9(4)
Se1	Sr1	$Se1^{5}$	133.56(4)	$Se6^{4}$	Mg3	Se4	79.7(3)
$Se1^{5}$	Sr1	$Se1^{3}$	86.13(9)	Se6	Mg3	Se4	79.7(3)
$Se1^{4}$	Sr1	$Se1^{3}$	86.13(9)	Se6	Mg3	$Se6^{4}$	89.2(4)
$Se1^{5}$	Sr1	$Se1^{1}$	133.56(4)	$Se6^{4}$	Mg3	Se11	86.4(4)
$Se1^{5}$	Sr1	$Se1^{4}$	86.13(9)	Se6	Mg3	Se11	86.4(4)
$Se1^{4}$	Sr1	$Se1^{1}$	133.56(4)	Se5	Mg4	Se2	100.2(4)
$Se1^{5}$	Sr1	$Se1^{2}$	75.91(12)	$Se5^{14}$	Mg4	Se2	100.2(4)
$Se10^{4}$	Sr2	$Se10^{9}$	86.22(9)	$Se5^{14}$	Mg4	Se5	94.4(4)
$Se10^{9}$	Sr2	$Se10^{6}$	75.79(12)	$Se5^{14}$	Mg4	Se6	177.9(4)
$Se10^{7}$	Sr2	Se10	86.22(9)	Se5	Mg4	Se6	87.75(8)
$Se10^{9}$	Sr2	Se10	133.52(4)	Se5	Mg4	$Se6^{14}$	177.9(4)
$Se10^{8}$	Sr2	Se10	133.52(4)	$Se5^{14}$	Mg4	$Se6^{14}$	87.75(8)
$Se10^{7}$	Sr2	$Se10^{4}$	133.52(4)	$Se5^{14}$	Mg4	Se7	92.8(4)
$Se10^{4}$	Sr2	$Se10^{6}$	133.52(4)	Se5	Mg4	Se7	92.8(4)
$Se10^{8}$	Sr2	$Se10^{6}$	133.52(4)	$Se6^{14}$	Mg4	Se2	79.4(4)
$Se10^{8}$	Sr2	$Se10^{4}$	86.22(9)	Se6	Mg4	Se2	79.4(4)
$Se10^{8}$	Sr2	$Se10^{7}$	75.79(12)	Se6	Mg4	$Se6^{14}$	90.1(4)
$Se10^{8}$	Sr2	$Se10^{9}$	86.22(9)	Se7	Mg4	Se2	160.8(5)
$Se10^{7}$	Sr2	$Se10^{6}$	86.22(9)	Se7	Mg4	Se6	87.1(4)
$Se10^{7}$	Sr2	$Se10^{9}$	133.52(4)	Se7	Mg4	$Se6^{14}$	87.1(4)
$Se10^{4}$	Sr2	Se10	75.79(12)	$Se3^{16}$	Mg5	$Se3^{10}$	92.4(5)
$Se10^{6}$	Sr2	Se10	86.22(9)	$Se3^{10}$	Mg5	Se7	82.1(4)
$Se5^{4}$	Sr3	$Se5^{10}$	133.41(3)	$Se3^{16}$	Mg5	Se7	82.1(4)
Se5	Sr3	$Se5^{13}$	133.41(3)	$Se3^{16}$	Mg5	$Se8^{7}$	85.0(3)
Se5	Sr3	$Se5^{10}$	86.46(8)	$Se3^{10}$	Mg5	$Se8^{7}$	85.0(3)
$Se5^{11}$	Sr3	Se5	86.46(8)	$Se8^{7}$	Mg5	Se7	161.3(6)
$Se5^{10}$	Sr3	$Se5^{13}$	75.47(10)	Se10	Mg5	$Se3^{16}$	178.0(5)
$Se5^{12}$	Sr3	$Se5^{10}$	133.41(4)	Se10	Mg5	$Se3^{10}$	85.98(9)
$Se5^{4}$	Sr3	$Se5^{13}$	86.45(8)	$Se10^{14}$	Mg5	$Se3^{16}$	85.98(9)
$Se5^{11}$	Sr3	$Se5^{12}$	75.47(10)	$Se10^{14}$	Mg5	$Se3^{10}$	178.0(5)
$Se5^{11}$	Sr3	$Se5^{10}$	86.45(8)	Se10	Mg5	Se7	98.8(3)
$Se5^{4}$	Sr3	Se5	75.47(10)	$Se10^{14}$	Mg5	Se7	98.8(3)

Se5[11]	Sr3	Se5[4]	133.42(3)	Se10[14]	Mg5	Se8[7]	93.8(4)
Se5[12]	Sr3	Se5[13]	86.45(8)	Se10	Mg5	Se8[7]	93.8(4)
Se5[11]	Sr3	Se5[13]	133.41(3)	Se10	Mg5	Se10[14]	95.6(5)
Se5[12]	Sr3	Se5[4]	86.46(8)	Se3[10]	Mg6	Se3[13]	91.5(5)
Se5[12]	Sr3	Se5	133.42(3)	Se3[13]	Mg6	Se9[7]	82.6(3)
Se1[4]	Mg1	Se1	93.8(4)	Se3[10]	Mg6	Se9[7]	82.6(3)
Se1[4]	Mg1	Se4[2]	90.2(4)	Se3[13]	Mg6	Se11	84.8(4)
Se1	Mg1	Se4[2]	90.2(4)	Se3[10]	Mg6	Se11	84.8(4)
Se1[4]	Mg1	Se6[5]	88.54(11)	Se10[4]	Mg6	Se3[13]	86.02(10)
Se1	Mg1	Se6[5]	168.0(6)	Se10	Mg6	Se3[13]	170.4(6)
Se1[4]	Mg1	Se6[2]	168.0(6)	Se10	Mg6	Se3[10]	86.02(10)
Se1	Mg1	Se6[2]	88.54(11)	Se10[4]	Mg6	Se3[10]	170.4(6)
Se1	Mg1	Se9[2]	106.2(4)	Se10[4]	Mg6	Se9[7]	87.9(4)
Se1[4]	Mg1	Se9[2]	106.2(4)	Se10	Mg6	Se9[7]	87.9(4)
Se6[5]	Mg1	Se4[2]	78.1(4)	Se10[4]	Mg6	Se10	94.9(5)
Se6[2]	Mg1	Se4[2]	78.1(4)	Se10	Mg6	Se11	104.2(4)
Se6[2]	Mg1	Se6[5]	86.8(4)	Se10[4]	Mg6	Se11	104.2(4)
Se9[2]	Mg1	Se4[2]	155.6(5)	Se11	Mg6	Se9[7]	161.9(6)
Se9[2]	Mg1	Se6[5]	84.3(3)	Se3	Ga1	Se7[11]	97.73(16)
Se9[2]	Mg1	Se6[2]	84.3(3)	Se3	Ga1	Se11[11]	99.48(17)
Se1[14]	Mg2	Se1	95.5(4)	Se5	Ga1	Se3	121.61(10)
Se1	Mg2	Se2[2]	95.5(4)	Se5	Ga1	Se7[11]	117.27(18)
Se1[14]	Mg2	Se2[2]	95.5(4)	Se5	Ga1	Se11[11]	112.96(19)
Se1	Mg2	Se6[2]	88.63(10)	Se7[11]	Ga1	Se11[11]	104.95(11)
Se1[14]	Mg2	Se6[2]	172.9(6)	Se6	Ga2	Se8	98.93(17)
Se1	Mg2	Se6[15]	172.9(6)	Se6	Ga2	Se9	100.58(16)
Se1[14]	Mg2	Se6[15]	88.63(10)	Se8	Ga2	Se9	104.89(10)
Se1[14]	Mg2	Se8[2]	102.6(4)	Se10	Ga2	Se6	125.54(10)
Se1	Mg2	Se8[2]	102.6(4)	Se10	Ga2	Se8	114.20(18)
Se2[2]	Mg2	Se6[2]	78.4(4)	Se10	Ga2	Se9	110.20(17)
Se2[2]	Mg2	Se6[15]	78.4(4)	Se1	Ga3	Se2	113.83(18)
Se2[2]	Mg2	Se8[2]	152.9(5)	Se1	Ga3	Se3	112.89(9)
Se6[15]	Mg2	Se6[2]	86.7(4)	Se1	Ga3	Se4	110.01(17)
Se8[2]	Mg2	Se6[15]	81.9(3)	Se2	Ga3	Se4	106.50(10)
Se8[2]	Mg2	Se6[2]	81.9(3)	Se3	Ga3	Se2	105.88(16)
Se4	Mg3	Se11	160.5(5)	Se3	Ga3	Se4	107.31(17)
Se5[4]	Mg3	Se4	104.2(4)				

[1]1+Y-X,1-X,+Z; [2]1-Y,+X-Y,+Z; [3]1+Y-X,1-X,1-Z; [4]+X,+Y,1-Z; [5]1-Y,+X-Y,1-Z; [6]1-Y,1+X-Y,+Z; [7]+Y-X,1-X,+Z; [8]+Y-X,1-X,1-Z; [9]1-Y,1+X-Y,1-Z; [10]-Y,+X-Y,+Z; [11]+Y-X,-X,+Z; [12]+Y-X,-X,1-Z; [13]-Y,+X-Y,1-Z; [14]+X,+Y,-Z; [15]1-Y,+X-Y,-Z; [16]-Y,+X-Y,-Z

Table S9. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $SrMg_6Ga_6Se_{16}$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr1	28.3(17)	28.3(17)	25(3)	0	0	14.1(8)
Sr2	26.0(18)	26.0(18)	27(3)	0	0	13.0(9)
Sr3	26.9(17)	26.9(17)	27(3)	0	0	13.5(8)
Mg1	24(6)	21(5)	30(5)	0	0	11(5)
Mg2	23(5)	28(6)	19(4)	0	0	13(5)
Mg3	25(5)	23(6)	22(5)	0	0	10(5)
Mg4	28(6)	35(6)	13(4)	0	0	19(5)
Mg5	33(7)	38(7)	16(5)	0	0	25(6)
Mg6	26(6)	19(5)	22(5)	0	0	14(5)
Ga1	20.1(9)	19.7(9)	19.3(9)	1.3(12)	0.0(11)	9.4(7)
Ga2	19.0(9)	19.0(8)	18.5(8)	-1.4(11)	2.1(12)	9.4(6)
Ga3	20.6(8)	18.8(9)	17.1(6)	-2.0(12)	-1.2(11)	9.9(8)
Se1	20.2(8)	21.1(9)	19.1(9)	2.0(11)	-0.3(12)	8.6(6)
Se2	20.0(18)	20.8(19)	16.5(14)	0	0	10.7(14)
Se3	17.9(17)	27(2)	20.0(16)	0	0	13.1(15)
Se4	16.9(7)	19.6(7)	19.6(7)	-0.3(12)	-0.6(11)	9.2(6)
Se5	20.0(18)	16.6(17)	18.9(19)	0	0	8.4(15)
Se6	23.9(8)	19.6(8)	20.5(8)	1.2(12)	1.5(15)	11.8(7)
Se7	19.1(19)	17.9(17)	18(2)	0	0	6.2(16)
Se8	18.2(8)	17.7(8)	19.0(7)	0.3(11)	-0.8(10)	8.6(6)
Se9	24.2(9)	20.4(8)	19.8(8)	-0.1(12)	1.5(16)	12.4(7)
Se10	21.5(17)	20(2)	14.6(14)	0	0	12.0(14)
Se11	15.3(15)	26(2)	18.1(15)	0	0	11.1(14)

Table S10. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence calculations for $BaMg_6Ga_6Se_{16}$.

Atom	Wyckoff	*x*	*y*	*z*	U(eq)	BVS[a)]
Ba1	1*c*	3333.33	6666.67	10000	23.5(6)	2.14
Ba2	1*e*	6666.67	3333.33	0	22.7(6)	2.14
Ba3	1*a*	0	0	0	20.6(6)	2.20
Ba4	1*b*	0	0	5000	28(5)	2.24
Mg1	3*k*	3750(6)	4626(5)	5000	19.7(17)	2.13
Mg2	3*k*	7117(6)	5823(6)	5000	23.1(18)	2.04
Mg3	3*j*	3852(6)	4656(6)	0	25(2)	2.06
Mg4	3*j*	7199(6)	5890(6)	0	24.5(17)	1.97
Mg5	3*k*	597(6)	2547(5)	0	23.5(18)	1.89
Mg6	3*j*	510(5)	2467(6)	5000	23.4(19)	1.99
Ga1	6*l*	5529.9(12)	6893.3(10)	7477(3)	17.7(4)	2.99
Ga2	6*l*	4785.9(11)	3634.3(12)	2539(3)	18.1(5)	2.95
Ga3	6*l*	2268.6(11)	1904.1(11)	2522(3)	16.8(3)	3.03
Se1	3*j*	5806.9(16)	7838(2)	10000	18.4(5)	1.79
Se2	6*l*	4095.3(12)	5732.8(12)	7489(2)	18.5(3)	2.17
Se3	3*k*	5895.6(16)	7863.5(18)	5000	16.4(5)	1.91
Se4	6*l*	6781.6(10)	6717.3(10)	7517(4)	16.3(3)	1.91
Se5	3*j*	5411(2)	4567(2)	0	18.6(5)	1.78
Se6	6*l*	4970.5(10)	2415.9(11)	2514(2)	19.7(3)	2.10
Se7	3*k*	5364(2)	4615(2)	5000	18.3(5)	1.89
Se8	6*l*	3331.3(9)	3432.2(9)	2489(4)	17.3(3)	2.19
Se9	6*l*	849.1(12)	1693.0(12)	2507.2(19)	20.0(3)	2.10
Se10	3*j*	2495.3(17)	1235(2)	0	18.7(5)	1.90
Se11	3*k*	2580.5(16)	1277(2)	5000	18.0(5)	1.97
GII[b)]				0.128		

[a)]The bond valence sum is calculated by bond-valence theory ($S_{ij} = \exp[(R_0\text{-}R)/B$, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and B= 0.37).

[b)]The global instability index (GII) calculated using

$$G = \sqrt{\frac{\sum_{i=1}^{n}(BVS - v_i)}{N}}$$

where N is the number of atoms in the formula unit. The GII is calculated as 0.128 which is lower than 0.2 indicating the rationality of the structure from this side.

Table S11. Selected bond lengths [Å] for $BaMg_6Ga_6Se_{16}$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ba1	Se2[6]	3.2606(16)	Mg3	Se1[23]	2.907(10)
Ba1	Se2	3.2605(16)	Mg3	Se2[20]	2.614(6)
Ba1	Se2[5]	3.2606(16)	Mg3	Se2[14]	2.614(6)
Ba1	Se2[7]	3.2606(16)	Mg3	Se5	2.847(9)
Ba1	Se2[4]	3.2606(16)	Mg3	Se8	2.705(7)
Ba1	Se2[8]	3.2606(16)	Mg3	Se8[13]	2.705(7)
Ba2	Se6[10]	3.2612(16)	Mg4	Se4[20]	2.742(6)
Ba2	Se6[9]	3.2611(16)	Mg4	Se4[14]	2.742(6)
Ba2	Se6[11]	3.2612(16)	Mg4	Se5	2.849(10)
Ba2	Se6[12]	3.2611(16)	Mg4	Se6[11]	2.651(6)
Ba2	Se6	3.2612(16)	Mg4	Se6[10]	2.651(6)
Ba2	Se6[13]	3.2612(16)	Mg4	Se10[10]	2.800(10)
Ba3	Se9[16]	3.2518(17)	Mg5	Se1[23]	2.749(9)
Ba3	Se9	3.2518(17)	Mg5	Se4[23]	2.816(6)
Ba3	Se9[17]	3.2518(17)	Mg5	Se4[24]	2.816(6)
Ba3	Se9[18]	3.2517(17)	Mg5	Se9[13]	2.643(6)
Ba3	Se9[13]	3.2517(17)	Mg5	Se9	2.643(6)
Ba3	Se9[15]	3.2517(17)	Mg5	Se10[15]	2.890(9)
Ba4	Se9	3.2451(17)	Mg6	Se3[4]	2.758(9)
Ba4	Se9[19]	3.2450(17)	Mg6	Se4[4]	2.831(6)
Ba4	Se9[20]	3.2450(17)	Mg6	Se4[24]	2.831(6)
Ba4	Se9[17]	3.2451(17)	Mg6	Se9[20]	2.616(6)
Ba4	Se9[21]	3.2451(17)	Mg6	Se9	2.616(6)
Ba4	Se9[15]	3.2450(17)	Mg6	Se11[15]	2.786(9)
Mg1	Se2[20]	2.605(6)	Ga1	Se1	2.467(3)
Mg1	Se2	2.605(6)	Ga1	Se2	2.339(2)
Mg1	Se3[4]	2.814(9)	Ga1	Se3	2.447(3)
Mg1	Se7	2.872(9)	Ga1	Se4	2.391(3)
Mg1	Se8[20]	2.700(6)	Ga2	Se5	2.458(3)
Mg1	Se8	2.700(6)	Ga2	Se6	2.342(2)
Mg2	Se4[20]	2.767(7)	Ga2	Se7	2.443(3)
Mg2	Se4	2.767(7)	Ga2	Se8	2.421(2)
Mg2	Se6[10]	2.625(6)	Ga3	Se8	2.406(2)
Mg2	Se6[22]	2.625(6)	Ga3	Se9	2.352(2)
Mg2	Se7	2.755(10)	Ga3	Se10	2.430(3)
Mg2	Se11[10]	2.816(10)	Ga3	Se11	2.426(3)

[1]+Y-X,1-X,1+Z; [2]1-Y,1+X-Y,1+Z; [3]+X,+Y,1+Z; [4]+Y-X,1-X,+Z; [5]1-Y,1+X-Y,+Z; [6]+Y-X,1-X,2-Z; [7]+X,+Y,2-Z; [8]1-Y,1+X-Y,2-Z; [9]1-Y,+X-Y,+Z; [10]1+Y-X,1-X,+Z; [11]1+Y-X,1-X,-Z; [12]1-Y,+X-Y,-Z; [13]+X,+Y,-Z; [14]+X,+Y,-1+Z; [15]-Y,+X-Y,+Z; [16]+Y-X,-X,-Z; [17]+Y-X,-X,+Z; [18]-Y,+X-Y,-Z; [19]-Y,+X-Y,1-Z; [20]+X,+Y,1-Z; [21]+Y-X,-X,1-Z; [22]1+Y-X,1-X,1-Z; [23]+Y-X,1-X,-1+Z; [24]+Y-X,1-X,1-Z

Table S12. Selected bond angles [°] for $BaMg_6Ga_6Se_{16}$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
$Se2^{5}$	Ba1	$Se2^{4}$	87.72(4)	$Se6^{22}$	Mg2	Se4	87.32(6)
$Se2^{5}$	Ba1	$Se2^{6}$	73.72(6)	$Se6^{10}$	Mg2	$Se6^{22}$	95.1(3)
$Se2^{5}$	Ba1	$Se2^{7}$	132.838(19)	$Se6^{10}$	Mg2	Se7	92.8(2)
$Se2^{6}$	Ba1	$Se2^{8}$	87.72(4)	$Se6^{22}$	Mg2	Se7	92.8(2)
$Se2^{6}$	Ba1	$Se2^{7}$	87.72(4)	$Se6^{22}$	Mg2	$Se11^{10}$	99.4(3)
Se2	Ba1	$Se2^{8}$	73.72(6)	$Se6^{10}$	Mg2	$Se11^{10}$	99.4(3)
$Se2^{5}$	Ba1	Se2	87.72(4)	Se7	Mg2	Se4	87.9(2)
$Se2^{6}$	Ba1	$Se2^{4}$	132.838(19)	Se7	Mg2	$Se4^{20}$	87.9(2)
$Se2^{6}$	Ba1	Se2	132.837(19)	Se7	Mg2	$Se11^{10}$	161.8(4)
$Se2^{7}$	Ba1	$Se2^{8}$	87.72(4)	$Se2^{14}$	Mg3	$Se1^{23}$	87.8(2)
$Se2^{7}$	Ba1	Se2	132.838(19)	$Se2^{20}$	Mg3	$Se1^{23}$	87.8(2)
$Se2^{7}$	Ba1	$Se2^{4}$	73.72(6)	$Se2^{20}$	Mg3	$Se2^{14}$	96.9(3)
$Se2^{4}$	Ba1	Se2	87.72(4)	$Se2^{14}$	Mg3	Se5	103.3(2)
$Se2^{5}$	Ba1	$Se2^{8}$	132.838(19)	$Se2^{20}$	Mg3	Se5	103.3(2)
$Se2^{4}$	Ba1	$Se2^{8}$	132.838(19)	$Se2^{20}$	Mg3	$Se8^{13}$	171.0(4)
$Se6^{9}$	Ba2	$Se6^{13}$	132.870(18)	$Se2^{20}$	Mg3	Se8	85.14(7)
$Se6^{10}$	Ba2	$Se6^{11}$	73.82(6)	$Se2^{14}$	Mg3	$Se8^{13}$	85.14(7)
$Se6^{9}$	Ba2	Se6	87.65(4)	$Se2^{14}$	Mg3	Se8	171.0(4)
$Se6^{9}$	Ba2	$Se6^{10}$	87.65(4)	Se5	Mg3	$Se1^{23}$	163.1(4)
$Se6^{9}$	Ba2	$Se6^{12}$	73.82(6)	$Se8^{13}$	Mg3	$Se1^{23}$	83.6(2)
$Se6^{9}$	Ba2	$Se6^{11}$	132.870(18)	Se8	Mg3	$Se1^{23}$	83.6(2)
Se6	Ba2	$Se6^{11}$	132.868(18)	$Se8^{13}$	Mg3	Se5	84.6(2)
$Se6^{12}$	Ba2	$Se6^{13}$	87.65(4)	Se8	Mg3	Se5	84.6(2)
$Se6^{13}$	Ba2	$Se6^{11}$	87.65(4)	Se8	Mg3	$Se8^{13}$	91.6(3)
Se6	Ba2	$Se6^{10}$	87.65(4)	$Se4^{20}$	Mg4	$Se4^{14}$	89.7(3)
$Se6^{12}$	Ba2	$Se6^{11}$	87.65(4)	$Se4^{20}$	Mg4	Se5	87.4(2)
Se6	Ba2	$Se6^{13}$	73.82(6)	$Se4^{14}$	Mg4	Se5	87.4(2)
$Se6^{13}$	Ba2	$Se6^{10}$	132.867(18)	$Se4^{20}$	Mg4	$Se10^{10}$	80.8(2)
$Se6^{12}$	Ba2	Se6	132.869(18)	$Se4^{14}$	Mg4	$Se10^{10}$	80.8(2)
$Se6^{12}$	Ba2	$Se6^{10}$	132.870(18)	$Se6^{10}$	Mg4	$Se4^{14}$	174.4(4)
$Se9^{15}$	Ba3	$Se9^{17}$	132.871(19)	$Se6^{11}$	Mg4	$Se4^{20}$	174.4(4)
Se9	Ba3	$Se9^{17}$	132.873(19)	$Se6^{11}$	Mg4	$Se4^{14}$	87.32(7)
$Se9^{13}$	Ba3	$Se9^{16}$	132.871(19)	$Se6^{10}$	Mg4	$Se4^{20}$	87.32(7)
$Se9^{13}$	Ba3	$Se9^{17}$	87.64(4)	$Se6^{11}$	Mg4	Se5	87.8(2)
$Se9^{18}$	Ba3	$Se9^{16}$	132.871(19)	$Se6^{10}$	Mg4	Se5	87.8(2)
$Se9^{17}$	Ba3	$Se9^{16}$	73.83(6)	$Se6^{11}$	Mg4	$Se6^{10}$	95.3(3)
$Se9^{15}$	Ba3	Se9	87.64(4)	$Se6^{11}$	Mg4	$Se10^{10}$	103.4(2)
$Se9^{18}$	Ba3	Se9	132.874(19)	$Se6^{10}$	Mg4	$Se10^{10}$	103.4(2)
$Se9^{18}$	Ba3	$Se9^{17}$	87.64(4)	$Se10^{10}$	Mg4	Se5	163.2(3)
Se9	Ba3	$Se9^{16}$	87.64(4)	$Se1^{23}$	Mg5	$Se4^{23}$	84.9(2)

Se9^{18}	Ba3	Se9^{15}	73.83(6)	Se1^{23}	Mg5	Se4^{24}	84.9(2)
Se9^{13}	Ba3	Se9	73.83(6)	Se1^{23}	Mg5	Se10^{15}	156.3(3)
Se9^{18}	Ba3	Se9^{13}	87.64(4)	Se4^{24}	Mg5	Se4^{23}	86.8(3)
Se9^{13}	Ba3	Se9^{15}	132.875(19)	Se4^{23}	Mg5	Se10^{15}	78.0(2)
Se9^{15}	Ba3	Se9^{16}	87.64(4)	Se4^{24}	Mg5	Se10^{15}	78.0(2)
Se9^{16}	Ba3	Se10^{16}	66.61(5)	Se9	Mg5	Se1^{23}	106.1(2)
Se9^{17}	Ba3	Se10^{16}	66.61(5)	Se9^{13}	Mg5	Se1^{23}	106.1(2)
Se9^{13}	Ba3	Se10^{16}	143.08(3)	Se9	Mg5	Se4^{23}	167.2(4)
Se9	Ba3	Se10^{16}	143.09(3)	Se9	Mg5	Se4^{24}	87.72(8)
Se9^{15}	Ba3	Se10^{16}	66.26(5)	Se9^{13}	Mg5	Se4^{23}	87.72(8)
Se9^{18}	Ba3	Se10^{16}	66.26(5)	Se9^{13}	Mg5	Se4^{24}	167.2(4)
Se10^{16}	Ba3	Se10^{15}	120	Se9	Mg5	Se9^{13}	95.3(3)
Se9^{15}	Ba4	Se9^{16}	87.87(4)	Se9	Mg5	Se10^{15}	89.6(2)
Se9^{20}	Ba4	Se9	73.51(6)	Se9^{13}	Mg5	Se10^{15}	89.6(2)
Se9^{15}	Ba4	Se9^{21}	73.51(6)	Se3^{5}	Mg6	Se4^{5}	82.7(2)
Se9^{15}	Ba4	Se9	87.87(4)	Se3^{5}	Mg6	Se4^{24}	82.7(2)
Se9^{15}	Ba4	Se9^{20}	132.772(19)	Se3^{5}	Mg6	Se11^{15}	154.2(3)
Se9	Ba4	Se9^{19}	132.769(19)	Se4^{5}	Mg6	Se4^{24}	87.7(3)
Se9	Ba4	Se9^{16}	87.87(4)	Se9^{20}	Mg6	Se3^{5}	102.2(2)
Se9^{20}	Ba4	Se9^{16}	132.768(19)	Se9	Mg6	Se3^{5}	102.2(2)
Se9^{19}	Ba4	Se9^{16}	73.51(6)	Se9^{20}	Mg6	Se4^{5}	87.93(7)
Se9^{21}	Ba4	Se9	132.770(19)	Se9^{20}	Mg6	Se4^{24}	172.9(3)
Se9^{21}	Ba4	Se9^{19}	87.87(4)	Se9	Mg6	Se4^{5}	172.9(3)
Se9^{21}	Ba4	Se9^{16}	132.768(19)	Se9	Mg6	Se4^{24}	87.93(7)
Se9^{20}	Ba4	Se9^{19}	87.87(4)	Se9	Mg6	Se9^{20}	95.9(3)
Se9^{20}	Ba4	Se9^{21}	87.87(4)	Se9	Mg6	Se11^{15}	94.9(2)
Se9^{15}	Ba4	Se9^{19}	132.768(19)	Se9^{20}	Mg6	Se11^{15}	94.9(2)
Se2^{20}	Mg1	Se2	96.2(3)	Se11^{15}	Mg6	Se4^{24}	78.7(2)
Se2	Mg1	Se3^{5}	92.9(2)	Se11^{15}	Mg6	Se4^{5}	78.7(2)
Se2^{20}	Mg1	Se3^{5}	92.9(2)	Se2	Ga1	Se1	110.72(11)
Se2^{20}	Mg1	Se7	98.4(2)	Se2	Ga1	Se3	114.27(11)
Se2	Mg1	Se7	98.4(2)	Se2	Ga1	Se4	123.87(9)
Se2	Mg1	Se8^{20}	85.43(7)	Se3	Ga1	Se1	104.96(9)
Se2^{20}	Mg1	Se8^{20}	177.6(3)	Se4	Ga1	Se1	101.27(11)
Se2	Mg1	Se8	177.6(3)	Se4	Ga1	Se3	99.51(11)
Se2^{20}	Mg1	Se8	85.43(7)	Se6	Ga2	Se5	112.95(11)
Se3^{5}	Mg1	Se7	163.1(3)	Se6	Ga2	Se7	117.46(11)
Se8^{20}	Mg1	Se3^{5}	85.4(2)	Se6	Ga2	Se8	119.57(10)
Se8	Mg1	Se3^{5}	85.4(2)	Se7	Ga2	Se5	105.36(11)
Se8^{20}	Mg1	Se7	83.0(2)	Se8	Ga2	Se5	100.08(12)
Se8	Mg1	Se7	83.0(2)	Se8	Ga2	Se7	98.92(12)
Se8	Mg1	Se8^{20}	92.9(3)	Se8	Ga3	Se10	108.28(11)
Se4^{20}	Mg2	Se4	90.3(3)	Se8	Ga3	Se11	107.17(11)

Se4	Mg2	Se11[10]	79.3(2)	Se9	Ga3	Se8	110.63(9)
Se4[20]	Mg2	Se11[10]	79.3(2)	Se9	Ga3	Se10	110.09(11)
Se6[22]	Mg2	Se4[20]	177.5(3)	Se9	Ga3	Se11	113.70(11)
Se6[10]	Mg2	Se4	177.5(3)	Se11	Ga3	Se10	106.75(9)
Se6[10]	Mg2	Se4[20]	87.32(6)				

[1]+Y-X,1-X,1+Z; [2]1-Y,1+X-Y,1+Z; [3]+X,+Y,1+Z; [4]+Y-X,1-X,+Z; [5]1-Y,1+X-Y,+Z; [6]+Y-X,1-X,2-Z; [7]+X,+Y,2-Z; [8]1-Y,1+X-Y,2-Z; [9]1-Y,+X-Y,+Z; [10]1+Y-X,1-X,+Z; [11]1+Y-X,1-X,-Z; [12]1-Y,+X-Y,-Z; [13]+X,+Y,-Z; [14]+X,+Y,-1+Z; [15]-Y,+X-Y,+Z; [16]+Y-X,-X,-Z; [17]+Y-X,-X,+Z; [18]-Y,+X-Y,-Z; [19]-Y,+X-Y,1-Z; [20]+X,+Y,1-Z; [21]+Y-X,-X,1-Z; [22]1+Y-X,1-X,1-Z; [23]+Y-X,1-X,-1+Z; [24]+Y-X,1-X,1-Z

Table S13. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $BaMg_6Ga_6Se_{16}$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba1	22.8(9)	22.8(9)	24.9(14)	0	0	11.4(4)
Ba2	23.2(8)	23.2(8)	21.7(13)	0	0	11.6(4)
Ba3	19.0(9)	19.0(9)	23.8(14)	0	0	9.5(4)
Mg1	31(5)	15(4)	14(3)	0	0	12(4)
Mg2	24(4)	22(4)	19(3)	0	0	9(3)
Mg3	32(5)	21(5)	12(3)	0	0	7(4)
Mg4	28(5)	15(4)	31(4)	0	0	11(4)
Mg5	30(4)	20(4)	23(4)	0	0	14(3)
Mg6	25(5)	26(4)	24(4)	0	0	17(4)
Ga1	17.6(8)	18.5(9)	16.7(6)	-0.6(8)	1.4(8)	8.9(7)
Ga2	19.0(9)	18.2(8)	17.7(7)	-0.7(8)	-0.5(8)	9.7(6)
Ga3	16.4(7)	18.6(8)	16.2(6)	1.0(7)	-0.7(7)	9.4(7)
Se1	20.1(13)	21.5(12)	16.5(10)	0	0	12.5(10)
Se2	17.8(7)	16.4(7)	18.9(7)	-3.0(8)	-0.2(8)	6.7(6)
Se3	19.2(12)	14.6(11)	16.7(9)	0	0	9.6(9)
Se4	15.8(7)	15.8(7)	17.8(7)	0.0(7)	-1.1(7)	8.5(6)
Se5	19.3(11)	15.4(11)	16.3(10)	0	0	5.1(11)
Se6	23.2(8)	17.4(7)	18.9(8)	-0.3(8)	2.1(7)	10.5(7)
Se7	17.1(11)	19.6(13)	16.1(10)	0	0	7.8(10)
Se8	17.0(6)	16.1(7)	17.9(5)	-0.2(7)	0.7(6)	7.5(5)
Se9	18.0(7)	24.0(8)	20.7(6)	-1.2(8)	-2.5(8)	12.4(7)
Se10	23.4(13)	21.2(13)	16.6(10)	0	0	15.0(11)
Se11	21.7(13)	16.9(12)	17.1(10)	0	0	11.0(10)

Table S14. The optical propertied of $A^{II}Mg_6Ga_6Se_{16}$ (A^{II} = Ca, Sr, Ba).

Compounds	Band gaps (eV)			Calculated NLO coefficients (pm/V)	Δn (@ 1064 nm)
	Experimental	GGA	HSE06		
$CaMg_6Ga_6Se_{16}$	2.71	1.851	2.568	d_{11} =-11.05, d_{22} =3.92	0.052
$SrMg_6Ga_6Se_{16}$	2.71	1.866	2.564	d_{11} =-10.67, d_{22} =3.93	0.048
$BaMg_6Ga_6Se_{16}$	2.69	1.853	2.556	d_{11} =-10.58, d_{22} =3.71	0.044

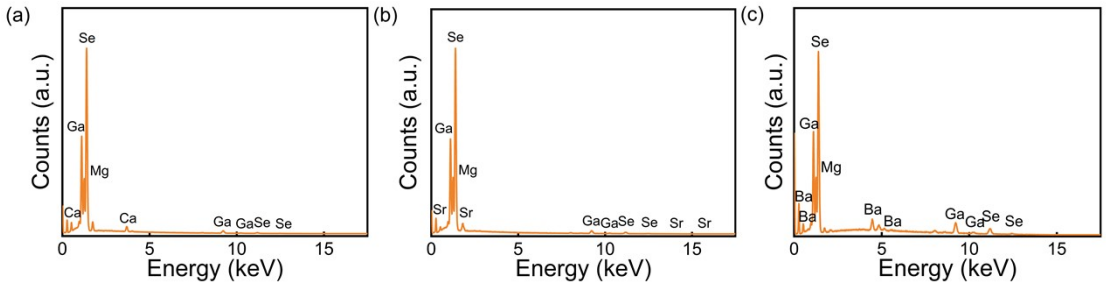

Figure S1. The EDS spectra of (a) $CaMg_6Ga_6Se_{16}$; (b) $SrMg_6Ga_6Se_{16}$; (c) $BaMg_6Ga_6Se_{16}$.

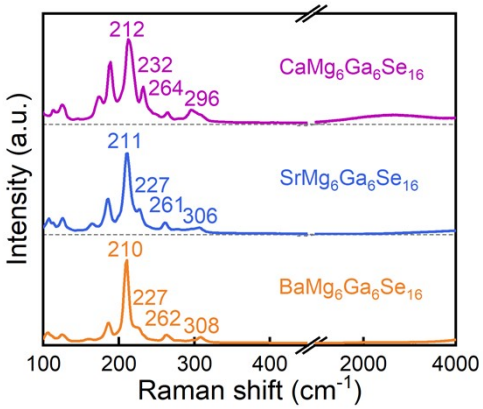

Figure S2. The Raman spectra of $A^{II}Mg_6Ga_6Se_{16}$ (A^{II} = Ca, Sr, Ba).

The peaks below 200 cm^{-1} can be attributed to the vibration of Mg–Se bonding in $[MgSe_6]$.[13] And the peaks at 212, 232, 264, and 296 cm^{-1} in $CaMg_6Ga_6Se_{16}$, 211, 227, 261, and 306 cm^{-1} in $SrMg_6Ga_6Se_{16}$, 210, 227, 262, and 308 cm^{-1} in $BaMg_6Ga_6Se_{16}$ can be attributed tothe vibration of Mg–Se bonding in $[GaSe_4]$.[13]

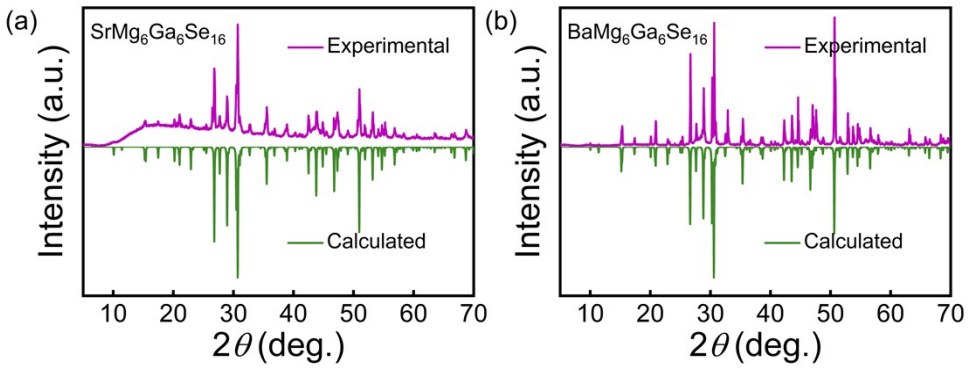

Figure S3. The XRD patterns of (a) $SrMg_6Ga_6Se_{16}$; (b) $BaMg_6Ga_6Se_{16}$.

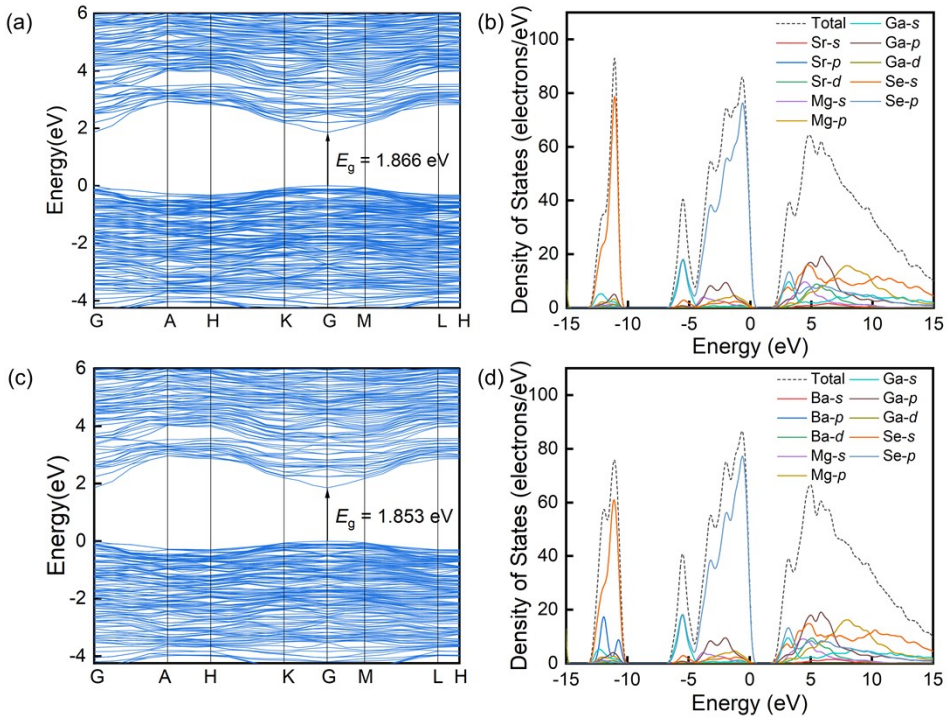

Figure S4. The band structures, total and partial density of states of $SrMg_6Ga_6Se_{16}$ (a,b); $BaMg_6Ga_6Se_{16}$ (c,d).

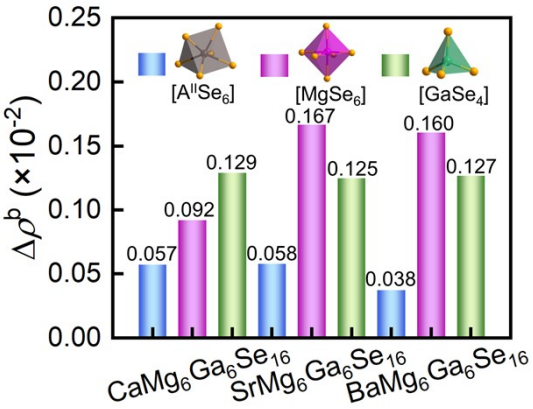

Figure S5. The bonding electron density differences ($\Delta\rho^b$) of [$A^{II}Se_6$] triangular prisms, [$MgSe_6$] octahedra and [$GaSe_4$] tetrahedra in $A^{II}Mg_6Ga_6Se_{16}$ calculated by REDA method.

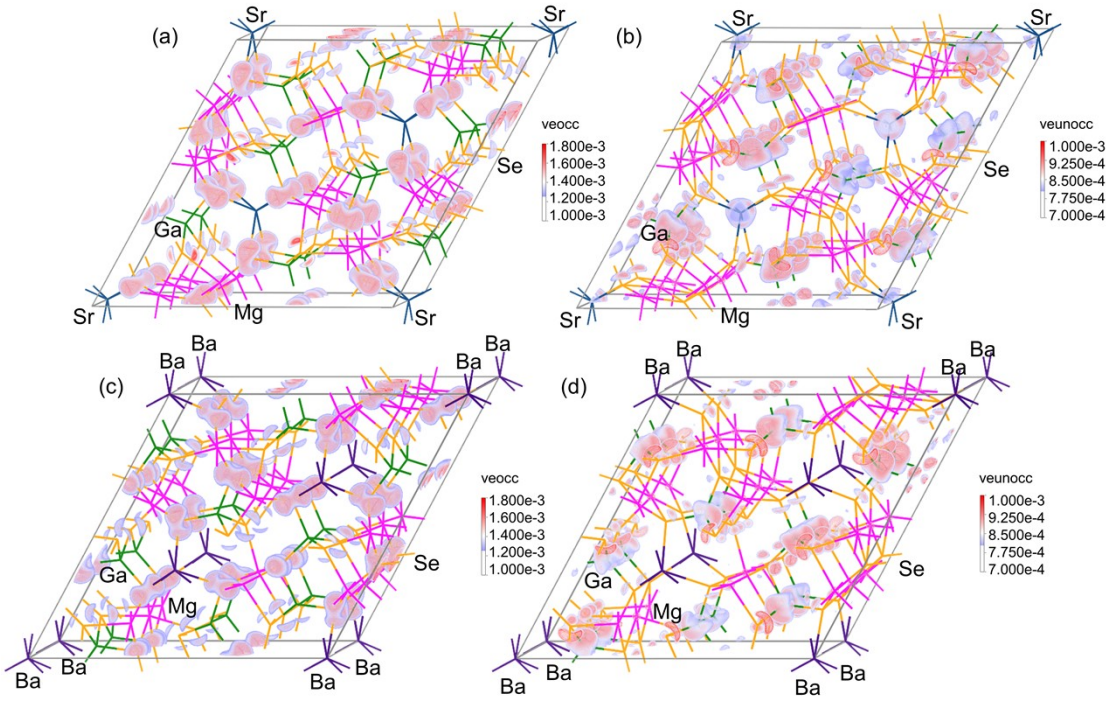

Figure S6. SHG density maps of occupied and unoccupied orbitals in the VE process. (a,b) $SrMg_6Ga_6Se_{16}$; (c,d) $BaMg_6Ga_6Se_{16}$.

Reference

1 J. Z. Zhou, L. A. Wang, Y. Chu, H. S. Wang, S. L. Pan and J. J. Li, *Adv. Opt. Mater.*, 2023, **11**, 2300736.

2 L. A. Wang, C. C. Tu, J. Z. Zhou, Y. Chu, Z. H. Yang, S. L. Pan and J. J. Li, *Adv. Opt. Mater.*, 2024, **12**, 2301634.

3 M. Mutailipu, M. Zhang, B. B. Zhang, L. Y. Wang, Z. H. Yang, X. Zhou and S. L. Pan, *Angew. Chem. Int. Ed.*, 2018, **57**, 6095–6099.

4 H. S. Wang, Y. Chu, X. T. Pan, Z. H. Yang, S. L. Pan and J. J. Li, *Mater. Today Phys.*, 2023, **38**, 101243.

5 X. F. Wang, Y. Wang, B. B. Zhang, F. F. Zhang, Z. H. Yang and S. L. Pan, *Angew. Chem. Int. Ed.*, 2017, **56**, 14119–14123.

6 J. J. Li, Z. Lian, Q. Li, Z. C. Wang, L. F. Liu, F. L. Deepak, Y. P. Liu, B. Li, J. Y. Xu and Z. X. Chen, *Nano Res.*, 2022, **15**, 5933–5939.

7 Y. Wang, B. B. Zhang, Z. H. Yang and S. L. Pan, *Angew. Chem. Int. Ed.*, 2018, **57**, 2150–2154.

8 B. B. Zhang, G. Q. Shi, Z. H. Yang, F. F. Zhang and S. L. Pan, *Angew. Chem. Int. Ed.*, 2017, **56**, 3916–3919.

9 Y. Chu, P. Wang, H. Zeng, S. C. Cheng, X. Su, Z. H. Yang, J. J. Li and S. L. Pan, *Chem. Mater.*, 2021, **33**, 6514–6521.

10 L. A. Wang, C. C. Tu, H. B. Gao, J. Z. Zhou, H. S. Wang, Z. H. Yang, S. L. Pan and J. J. Li, *Sci. China Chem.*, 2023, **66**, 1086–1093.

11 L. A. Wang, D. D. Chu, D. Q. Yin, C. W. Xie, Z. H. Yang, J. J. Li and S. L. Pan, *Mater. Today Phys.*, 2023, **38**, 101245.

12 B. H. Lei, Z. H. Yang, H. W. Yu, C. Cao, Z. Li, C. Hu, K. R. Poeppelmeier and S. L. Pan, *J. Am. Chem. Soc.*, 2018, **140**, 10726–10733.

13 P. Wang, Y. Chu, A. Tudi, C. W. Xie, Z. H. Yang, S. L. Pan and J. J. Li, *Adv. Sci.*, 2022, **9**, 2106120.