Supporting Information

Designing Infrared Nonlinear Optical Crystals, $Sr_2MgSn_2OS_6$ and $Sr_2SnGa_2OS_6$ with Hybrid Anionic Frameworks via Double Substitution Strategy

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Table S1. Crystal data and structure refinement for $Sr_2MgSn_2OS_6$ and $Sr_2SnGa_2OS_6$.

CCDC number	2402942	2402941
Empirical formula	$Sr_2MgSn_2OS_6$	$Sr_2SnGa_2OS_6$
Formula weight	645.36	641.791
Temperature [K]	293(2)	
Crystal system	tetragonal	
Space group (number)	$P\bar{4}2_1m$ (No. 113)	
a [Å]	9.5344(17)	9.5281(11)
b [Å]	9.5344(17)	9.5281(11)
c [Å]	6.2123(16)	6.2183(10)
Volume [Å^3]	564.7(2)	564.53(16)
Z	2	2
ρ_{calc} [gcm^{-3}]	3.809	3.775
μ [mm^{-1}]	14.933	17.336
Goodness-of-fit on F^2	1.072	0.821
Final *R* indexes [$I \geq 2\sigma(I)$] [a]	R_1 = 0.0525	R_1 = 0.0334
	wR_2 = 0.1055	wR_2 = 0.0692
Final *R* indexes [all data]	R_1 = 0.0649	R_1 = 0.0403
	wR_2 = 0.1114	wR_2 = 0.0736
Largest peak/hole [eÅ^{-3}]	1.22/-1.11	0.67/-0.83
Flack X parameter	0.59(5)	0.02(2)

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

Table S2. The atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Sr_2MgSn_2OS_6$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the BVS for each atom in the asymmetric unit of $Sr_2MgSn_2OS_6$.

Atom	Wyckoff position	x	y	z	U_{eq}	BVS
Sr(1)	*2a*	0.1521(2)	0.6521(2)	1.0131(4)	0.022(1)	2.09
Mg(1)	*4e*	0.1273(2)	0.3727(2)	0.4408(3)	0.017(1)	2.07
Mg(2)	*2b*	0.5000	0.5000	0.5000	0.015(1)	2.11
Sn(1)	*4e*	0.1273(2)	0.3727(2)	0.4408(3)	0.017(1)	3.93
Sn(2)	*2b*	0.5000	0.5000	0.5000	0.015(1)	3.89
O(1)	*1c*	0	0.5000	0.3030(30)	0.026(6)	2.05
S(1)	*4e*	0.1373(5)	0.3627(5)	0.7973(8)	0.020(1)	1.95
S(2)	*8f*	0.3322(5)	0.4312(5)	0.2561(6)	0.020(1)	1.98

Table S3. The atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Sr_2SnGa_2OS_6$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the BVS for each atom in the asymmetric unit of $Sr_2SnGa_2OS_6$.

Atom	Wyckoff position	x	y	z	U_{eq}	BVS
Sr(1)	*2a*	0.8478(1)	0.3478(1)	-0.0128(2)	0.017(1)	2.12
Sn(1)	*4e*	0.8724(1)	0.6276(1)	0.5591(2)	0.012(1)	3.89
Sn(2)	*2b*	0.5000	0.5000	0.5000	0.012(1)	3.93
Ga(1)	*4e*	0.8724(1)	0.6276(1)	0.5591(2)	0.012(1)	3.12
Ga(2)	*2b*	0.5000	0.5000	0.5000	0.012(1)	3.07
O(1)	*1c*	1.0000	0.5000	0.7000(20)	0.014(3)	1.96
S(1)	*4e*	0.8627(3)	0.6373(3)	0.2025(6)	0.016(1)	2.05
S(2)	*8f*	0.6680(3)	0.5684(3)	0.7436(4)	0.014(1)	2.09

Table S4. Selected lengths (Å) and bond angles (°) for $Sr_2MgSn_2OS_6$.

Atom–Atom	**Length [Å]**
Sr(1)-O(1)$^{\#1}$	2.732(14)
Sr(1)-S(1)$^{\#2}$	3.074(6)
Sr(1)-S(1)	3.071(5)
Sr(1)-S(1)$^{\#3}$	3.071(5)
Sr(1)-S(2)$^{\#4}$	3.108(5)
Sr(1)-S(2)$^{\#1}$	3.108(5)
Sr(1)-S(2)$^{\#5}$	3.146(5)
Sr(1)-S(2)$^{\#6}$	3.146(5)
Sr(1)-Sn(1)$^{\#7}$	3.770(3)
Sr(1)-Sn(1)$^{\#1}$	3.770(3)
Sr(1)-Mg(1)$^{\#5}$	4.099(3)
Sr(1)-Sr(1)$^{\#3}$	4.102(5)
S(1)-Sn(1)	2.218(5)
S(2)-Sn(2)	2.299(4)
S(2)-Sn(1)	2.334(5)
O(1)-Sn(1)	1.916(10)
O(1)-Sn(1)$^{\#3}$	1.917(10)
Atom–Atom–Atom	**Angle [°]**
O(1)$^{\#1}$-Sr(1)-S(1)$^{\#2}$	116.1(4)
O(1)$^{\#1}$-Sr(1)-S(1)	77.7(3)
S(1)$^{\#2}$-Sr(1)-S(1)	141.65(9)
O(1)$^{\#1}$-Sr(1)-S(1)$^{\#3}$	77.7(3)
S(1)$^{\#2}$-Sr(1)-S(1)$^{\#3}$	141.65(9)
S(1)-Sr(1)-S(1)$^{\#3}$	74.1(2)
O(1)$^{\#1}$-Sr(1)-S(2)$^{\#4}$	67.22(14)
S(1)$^{\#2}$-Sr(1)-S(2)$^{\#4}$	84.02(11)
S(1)-Sr(1)-S(2)$^{\#4}$	132.61(14)
S(1)$^{\#3}$-Sr(1)-S(2)$^{\#4}$	68.20(13)
O(1)$^{\#1}$-Sr(1)-S(2)$^{\#1}$	67.22(15)
S(1)$^{\#2}$-Sr(1)-S(2)$^{\#1}$	84.02(11)
S(1)-Sr(1)-S(2)$^{\#1}$	68.20(13)
S(1)$^{\#3}$-Sr(1)-S(2)$^{\#1}$	132.61(14)
S(2)$^{\#4}$-Sr(1)-S(2)$^{\#1}$	120.84(17)
O(1)$^{\#1}$-Sr(1)-S(2)$^{\#5}$	145.62(8)
S(1)$^{\#2}$-Sr(1)-S(2)$^{\#5}$	67.68(12)
S(1)-Sr(1)-S(2)$^{\#5}$	81.36(12)
S(1)$^{\#3}$-Sr(1)-S(2)$^{\#5}$	122.01(14)
S(2)$^{\#4}$-Sr(1)-S(2)$^{\#5}$	143.60(9)
S(2)$^{\#1}$-Sr(1)-S(2)$^{\#5}$	79.82(16)
O(1)$^{\#1}$-Sr(1)-S(2)$^{\#6}$	145.62(9)
S(1)$^{\#2}$-Sr(1)-S(2)$^{\#6}$	67.68(12)
S(1)-Sr(1)-S(2)$^{\#6}$	122.01(14)
S(1)$^{\#3}$-Sr(1)-S(2)$^{\#6}$	81.36(12)
S(2)$^{\#4}$-Sr(1)-S(2)$^{\#6}$	79.82(16)
S(2)$^{\#1}$-Sr(1)-S(2)$^{\#6}$	143.60(9)
S(2)$^{\#5}$-Sr(1)-S(2)$^{\#6}$	68.72(17)
O(1)-Sn(1)-S(1)	119.9(6)
O(1)-Sn(1)-S(2)	99.2(4)
S(1)-Sn(1)-S(2)	117.73(16)
O(1)-Sn(1)-S(2)$^{\#12}$	99.2(4)
S(1)-Sn(1)-S(2)$^{\#12}$	117.73(15)
S(2)-Sn(1)-S(2)$^{\#12}$	99.1(2)
S(2)$^{\#5}$-Sn(2)-S(2)$^{\#10}$	97.5(2)
S(2)$^{\#5}$-Sn(2)-S(2)$^{\#13}$	115.74(12)
S(2)$^{\#10}$-Sn(2)-S(2)$^{\#13}$	115.74(12)
S(2)$^{\#5}$-Sn(2)-S(2)	115.74(12)
S(2)$^{\#10}$-Sn(2)-S(2)	115.74(12)
S(2)$^{\#13}$-Sn(2)-S(2)	97.5(2)

Symmetry transformations used to generate equivalent atoms:

#1: x, y, z+1; #2: y, -x+1, -z+2; #3: -x, -y+1, z; #4: y-1/2, x+1/2, z+1; #5: y, -x+1, -z+1; #6: -x+1/2, y+1/2, -z+1; #7: -x, -y+1, z+1; #8: -y+1, x, -z+2; #9: x, y, z-1; #10: -y+1, x, -z+1; #11: -x, -y+1, z-1; #12: -y+1/2, -x+1/2, z; #13: -x+1, -y+1, z;

Table S5. Selected lengths (Å) and bond angles (°) for $Sr_2SnGa_2OS_6$.

Atom–Atom	**Length [Å]**
Sr(1)-O(1)$^{\#1}$	2.719(9)
Sr(1)-S(1)	3.070(3)
Sr(1)-S(1)$^{\#2}$	3.070(3)
Sr(1)-S(1)$^{\#3}$	3.072(4)
Sr(1)-S(2)$^{\#4}$	3.106(3)
Sr(1)-S(2)$^{\#1}$	3.106(3)
Sr(1)-S(2)$^{\#5}$	3.148(3)
Sr(1)-S(2)$^{\#6}$	3.148(3)
Sr(1)-Ga(1)$^{\#1}$	3.7740(18)
Sr(1)-Ga(1)$^{\#7}$	3.7740(18)
Sr(1)-Sr(1)$^{\#2}$	4.101(3)
Ga(1)-O(1)	1.929(7)
Ga(1)-S(1)	2.221(4)
Ga(1)-S(2)$^{\#8}$	2.330(3)
Ga(1)-S(2)	2.330(3)
Ga(2)-S(2)	2.298(3)
Ga(2)-S(2)$^{\#9}$	2.298(3)
Ga(2)-S(2)$^{\#6}$	2.298(3)
Ga(2)-S(2)$^{\#10}$	2.298(3)
Atom–Atom–Atom	**Angle [°]**
O(1)$^{\#1}$-Sr(1)-S(1)	77.46(18)
O(1)$^{\#1}$-Sr(1)-S(1)$^{\#2}$	77.46(18)
S(1)-Sr(1)-S(1)$^{\#2}$	74.15(13)
O(1)$^{\#1}$-Sr(1)-S(1)$^{\#3}$	116.4(2)
S(1)-Sr(1)-S(1)$^{\#3}$	141.66(6)
S(1)$^{\#2}$-Sr(1)-S(1)$^{\#3}$	141.66(6)
O(1)$^{\#1}$-Sr(1)-S(2)$^{\#4}$	67.23(10)
S(1)-Sr(1)-S(2)$^{\#4}$	132.63(9)
S(1)$^{\#2}$-Sr(1)-S(2)$^{\#4}$	68.29(9)
S(1)$^{\#3}$-Sr(1)-S(2)$^{\#4}$	83.94(7)
O(1)$^{\#1}$-Sr(1)-S(2)$^{\#1}$	67.23(10)
S(1)-Sr(1)-S(2)$^{\#1}$	68.29(9)
S(1)$^{\#2}$-Sr(1)-S(2)$^{\#1}$	132.63(9)
S(1)$^{\#3}$-Sr(1)-S(2)$^{\#1}$	83.94(7)
S(2)$^{\#4}$-Sr(1)-S(2)$^{\#1}$	120.58(11)
O(1)$^{\#1}$-Sr(1)-S(2)$^{\#5}$	145.65(5)
S(1)-Sr(1)-S(2)$^{\#5}$	122.00(9)
S(1)$^{\#2}$-Sr(1)-S(2)$^{\#5}$	81.37(7)
S(1)$^{\#3}$-Sr(1)-S(2)$^{\#5}$	67.73(8)
S(2)$^{\#8}$-Ga(1)-S(2)	99.32(15)
S(2)$^{\#1}$-Sr(1)-S(2)$^{\#5}$	143.62(5)
O(1)$^{\#1}$-Sr(1)-S(2)$^{\#6}$	145.65(5)
S(1)-Sr(1)-S(2)$^{\#6}$	81.37(7)
S(1)$^{\#2}$-Sr(1)-S(2)$^{\#6}$	122.00(9)
S(1)$^{\#3}$-Sr(1)-S(2)$^{\#6}$	67.73(8)
S(2)$^{\#4}$-Sr(1)-S(2)$^{\#6}$	143.62(5)
S(2)$^{\#1}$-Sr(1)-S(2)$^{\#6}$	79.94(10)
S(2)$^{\#5}$-Sr(1)-S(2)$^{\#6}$	68.67(10)
O(1)-Ga(1)-S(1)	120.4(4)
O(1)-Ga(1)-S(2)$^{\#8}$	98.7(3)
S(1)-Ga(1)-S(2)$^{\#8}$	117.80(10)
O(1)-Ga(1)-S(2)	98.7(3)
S(1)-Ga(1)-S(2)	117.80(10)
O(1)-Ga(1)-S(1)	120.4(4)
O(1)-Ga(1)-S(2)$^{\#8}$	98.7(3)
S(1)-Ga(1)-S(2)$^{\#8}$	117.80(10)
O(1)-Ga(1)-S(2)	98.7(3)
S(1)-Ga(1)-S(2)	117.80(10)
S(2)-Ga(2)-S(2)$^{\#9}$	97.54(13)
S(2)-Ga(2)-S(2)$^{\#6}$	115.74(7)
S(2)$^{\#9}$-Ga(2)-S(2)$^{\#6}$	115.74(7)
S(2)-Ga(2)-S(2)$^{\#10}$	115.74(7)
S(2)$^{\#9}$-Ga(2)-S(2)$^{\#10}$	115.74(7)
S(2)$^{\#6}$-Ga(2)-S(2)$^{\#10}$	97.54(13)

Symmetry transformations used to generate equivalent atoms:

#1: x, y, z-1; #2: -x+2, -y+1, z; #3: y, -x+1, -z; #4: y+1/2, x-1/2, z-1; #5: -x+3/2, y-1/2, -z+1; #6: y, -x+1, -z+1; #7: -x+2, -y+1, z-1; #8: -y+3/2, -x+3/2, z; #9: x+1, -y+1, z; #10: -y+1, x, -z+1; #11: -x+2, -y+1, z+1; #12: x, y, z+1; #13: -y+1, x, -z;

Table S6. The space groups, Dipole moment, and the flexibility indices (F) of [SiO_4] and [(Sn/Ga)OS_3] units in $Sr_2MgSi_2O_7$, $Sr_2SnGa_2OS_6$.

Compounds	Space groups	Tetrahedral units	Dipole moment (Debye)	F
$Sr_2MgSi_2O_7$	$P\bar{4}2_1m$	[SiO_4]	1.97	0.102
$Sr_2SnGa_2OS_6$	$P\bar{4}2_1m$	[(Sn/Ga)OS_3]	8.72	0.178

Figure S1. Experimental (red) and simulated (black) powder XRD patterns of $Sr_2SnGa_2OS_6$.

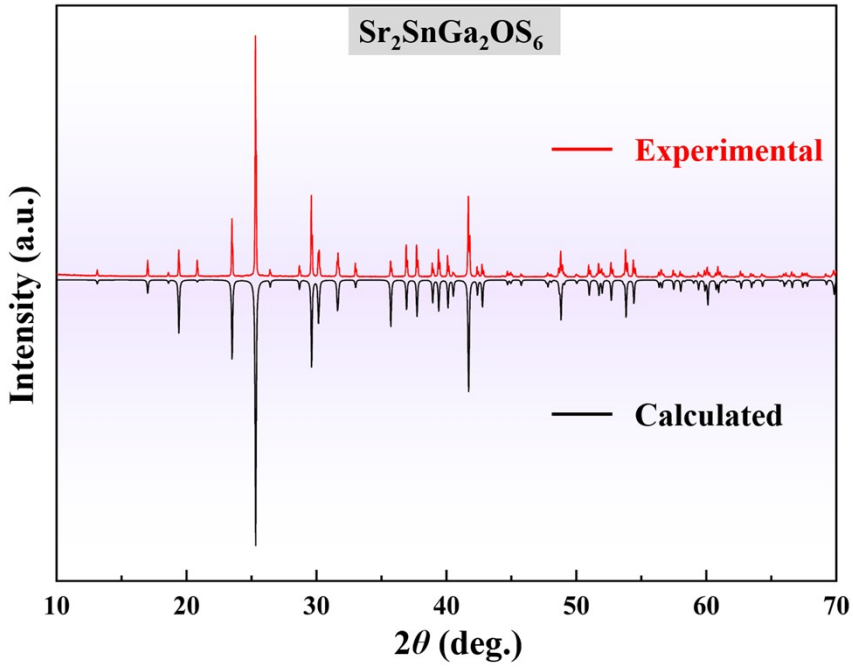

Figure S2. Experimental results (Dark blue) and simulated (red) powder XRD patterns of $Sr_2MgSn_2OS_6$.

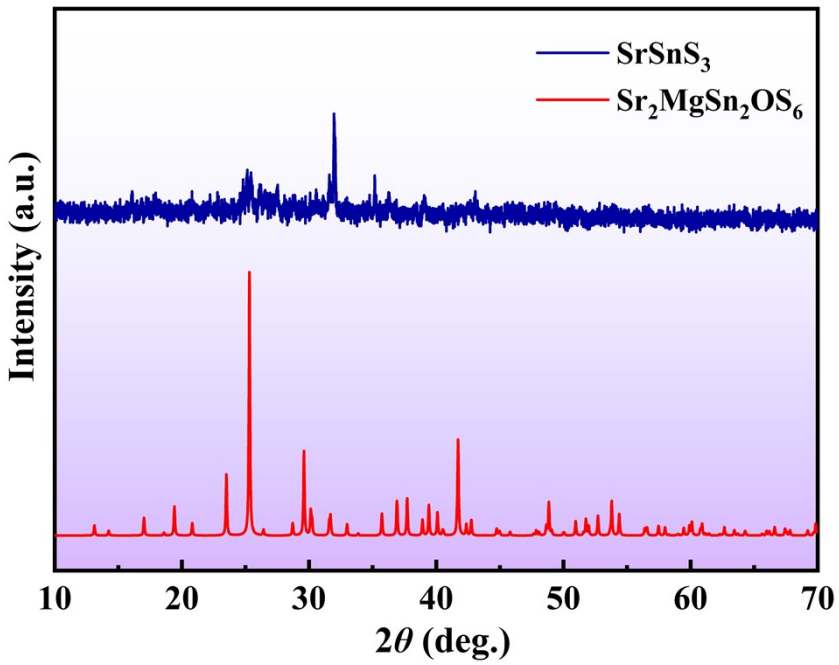

Figure S3. Experimental results [(1) blue and (2) purple] and simulated (red) powder XRD patterns of $Sr_2MgSn_2OS_6$.

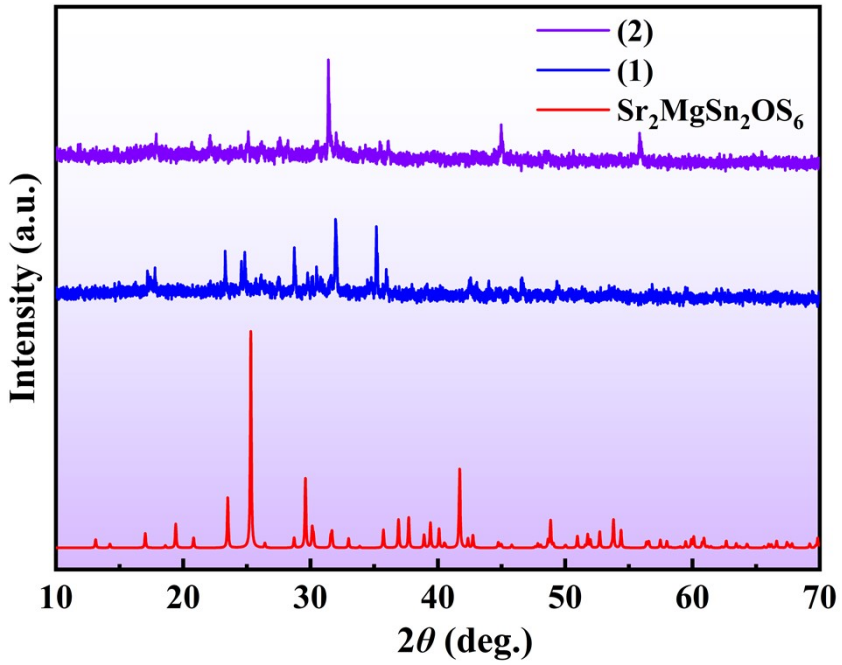

Figure S4. Experimental (red) and simulated (black) powder XRD patterns of $Sr_2MgSi_2O_7$.

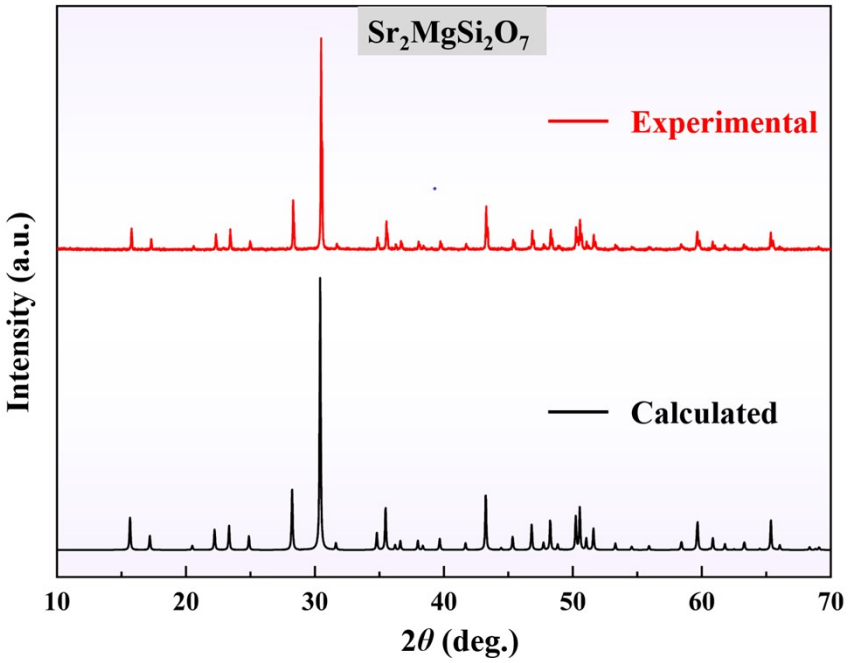

Figure S5. The variable-temperature powder XRD of the $Sr_2SnGa_2OS_6$.

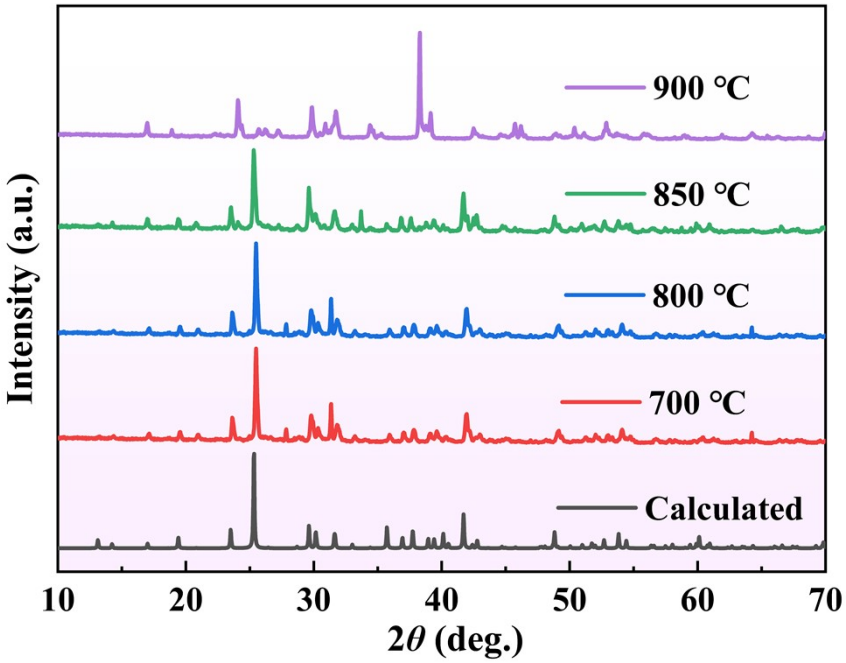

Figure S6. Shrinkage phenomenon of $Sr_2SnGa_2OS_6$ at different temperatures.

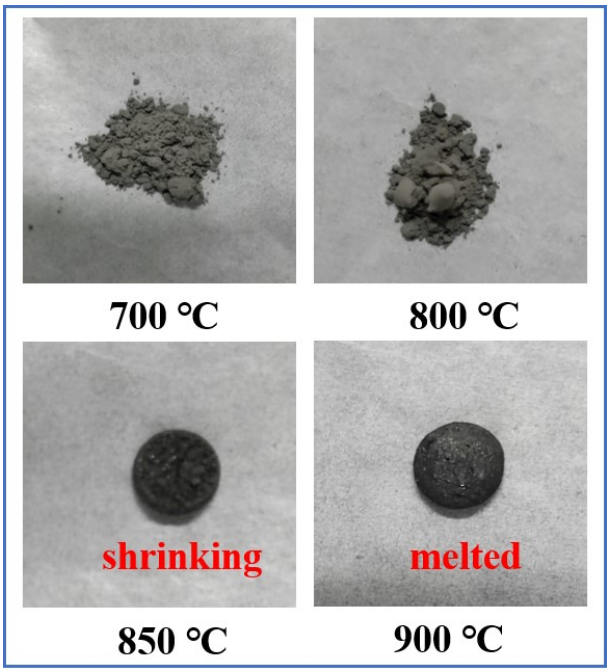

Figure S7. The IR transmittance spectrum of $Sr_2MgSi_2O_7$.

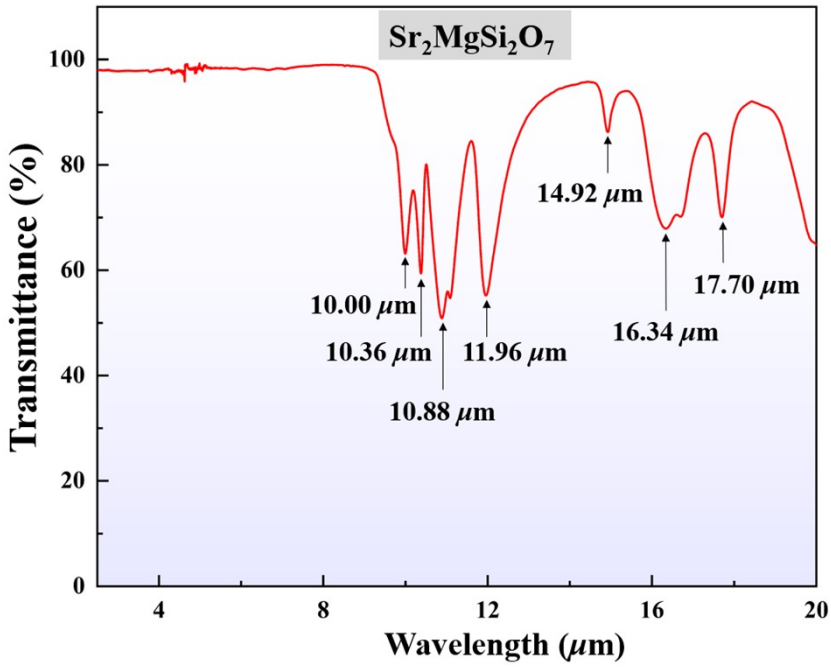

Figure S8. SHG signals of $Sr_2MgSi_2O_7$ with AGS as a reference at a particle size of 150−210 μm at 2090 nm radiation.