Supporting Information

Effectively Designing Infrared Nonlinear Optical Materials with Magnetism, $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb) Aided by the Stable Open Frameworks

Kaixuan Li [a], Yujie Zhang [a], Xianchao Zhu [a], Hongping Wu [a*], Zhanggui Hu [a], Jiyang Wang [a] and Yicheng Wu [a]*

[a] Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, Tianjin University of Technology, Tianjin 300384, China.

CONTENTS

Experimental Methods

Syntheses

$MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb) were synthesized by the conventional solid-state method. The initial reagents including CaS (Aladdin, 99.9%), SrS (Aladdin, 99.5%), BaS (Aladdin, 99 %), PbS (Aladdin, 99.9%), MnS (Aladdin, 99.9%), Ga_2S_3 (Aladdin, 95%) and S (Aladdin, 99%) were used without further purification. Stoichiometric amounts of reactants were mixed thoroughly and heated in the corundum crucibles. The reactants, reaction time, and temperature for all compound are listed below.

$MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb): $CaMn_6Ga_6S_{16}$ was synthesized using CaS (0.0273 g), MnS (0.1977 g), Ga_2S_3 (0.2543g), and S (0.0206g). After weighing the raw materials, they were ground evenly, and loaded into a small graphite crucible, and then the crucibles were flame-sealed under a pressure of 10^{-3} Pa in a fused-silica tube. The mixtures were heated from room temperature to 950 C in 15 h, held at that temperature for 40 h, cooled to 900 °C in 50 h, and finally cooled to room temperature in 24 h. $SrMn_6Ga_6S_{16}$, $BaMn_6Ga_6S_{16}$ and $PbMn_6Ga_6S_{16}$ were also successfully synthesized under identical conditions.

Single Crystal X-ray Diffraction

Single-crystal data was collected on a Bruker SMART APEX III 4 K CCD diffractometer using Mo-Kα (λ =0.71073 Å) radiation at 293(2) K. The structure of three crystals were solved directly by the SHELXTL crystallographic software package and all atoms were refined by the full-matrix least squares technique. The final structures were examined for the presence of any missing symmetry elements using PLATON, and no additional higher symmetry elements were identified. The crystal data and structure refinement details are listed in Table S1 and the atomic coordination, displacement parameters, bond valence sums (BVSs), and selected bond lengths and angles are summarized in Tables S2

Powder XRD

$MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb) were tested using a SmartLab9KW powder X-ray diffractometer. The experimental XRD spectra of the title compounds were measured using X-rays with Cu Kα radiation (λ = 1.541 Å) at room temperature, and the measurement results show that the PXRD patterns of the as-synthesized samples match the calculated ones derived from their single crystal data. The results of refining powder by the Rietveld method are in reasonable ranges, indicating the high purity and crystallinity of the as-prepared samples. The fitted profile matches the experimental data well, giving the acceptance R values of Rp = 0.08 for $CaMn_6Ga_6S_{16}$, respectively, with all of the observed Bragg reflections indexed into the space group of $P\bar{6}$.

Infrared spectroscopy

The IR spectra of $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb) were recorded on a Nicolet iS50 Fourier transform infrared (FTIR) spectrometer in the range of 600–4000 cm^{-1}. The silicates were ground and mixed with KBr.

UV-vis-NIR diffuse-reflectance spectra

The UV-vis-NIR diffuse reflectance spectra of $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb) were measured at room temperature with a Shimadzu SolidSpec-3700DUV spectrophotometer. The wavelengths of the spectra were in the range 240–2000 nm. Absorption (K/S) data were calculated from the following Kubelka–Munk function: $F(R) = (1-R)^2/2R = K/S$, R represents the reflectance, K the absorption, and S the scattering factor.

Birefringence measurement.

The birefringence was measured using a Nikon Eclipse polarizing microscope E200MV POL with a halogen lamp. According to the formula $R = \Delta n \times d$, where R, Δn, and d represent optical path difference, birefringence, and thickness, respectively. The birefringence was calculated by measuring the optical path compared with the Michel-Levy chart and the thickness with a Bruker SMART APEX II. The transparent $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb) crystal was selected for the measurement to ensure the result's precision.

SHG measurement

The SHG responses were measured based on the Kurtz–Perry method by irradiation of a 2090 nm Q-switched laser (50 ns, 3 Hz) with the AGS as a reference. Further, their effective NLO coefficients d_{eff} were calculated using the formula $d_{eff} = d_{eff,\ AGS}\ (I^{2\omega}/I^{2\omega}{}_{AGS})^{1/2}$ ($I^{2\omega}$ and $I^{2\omega}{}_{AGS}$ are SHG intensities for sample and AGS, respectively) with polycrystalline $d_{eff,\ AGS}$ = 11.8 pm V^{-1}(polycrystalline $d_{eff,\ AGS}$ is the angular average of single-crystal $d_{36,\ AGS}$ = 13.7 pm V^{-1}).

Laser damage threshold measurement.

The LDTs of the $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb) and AGS powder at the particle size range of 180−250 μm were evaluated under using high-power laser irradiation of 1064 nm (pulse width τ_p = 10 ns) by the single-pulse method. The measurement processes were performed by gradually increasing the laser power until the damaged spot was observed under a microscope. The damage thresholds were derived from the equation $I_{(threshold)}=E/(\pi r^2 \tau_p)$, where Eis the laser energy of a single pulse, r is the spot radius, and τ_p is the pulse width.

Magnetic properties measurement

The temperature dependence of magnetization (M-T) of $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb) powder are investigated after zero-field cooling (ZFC) and field cooling (FC) processes under an applied field of H = 5000 Oe utilizing a physical properties measurement system (PPMS 9 T, Quantum Design).

Table S1. Crystallographic Data and Refinement Details for $CaMn_6Ga_6S_{16}$, $SrMn_6Ga_6S_{16}$, $BaMn_6Ga_6S_{16}$ and $PbMn_6Ga_6S_{16}$.

Empirical formula	$CaMn_6Ga_6S_{16}$	$SrMn_6Ga_6S_{16}$	$BaMn_6Ga_6S_{16}$	$PbMn_6Ga_6S_{16}$
Formula weight	1301.00	1348.54	1398.26	1468.11
Temperature	297(2) K			
Crystal system	Hexagonal			
Space group	$P\bar{6}$			
Z	3			
a (Å)	16.7529(7)	16.8606(5)	16.9985(5)	16.8215(3)
c (Å)	7.4170(5)	7.4237(3)	7.4406(4)	7.4281(2)
V (Å^3)	1802.76(19)	1827.67(13)	1861.91(15)	1820.28
D_c (g cm^{-3})	3.595	3.676	3.741	4.018
μ (mm^{-1})	11.236	13.038	12.226	17.821
F (000)	1836	1890	1944	2022
Crystal size (mm^3)	0.258 x 0.135 x 0.105	0.222 x 0.075 x 0.049	0.121 x 0.117 x 0.063	0.258 x 0.135 x 0.105
Radiation	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)
2θ range (°)	2.43 to 25.02	2.41 to 25.00	2.39 to 25.02	2.42 to 25.01
Reflections collected	13489	10981	14168	12016
Indep. Reflns/ Rint	2300 / 0.0420	2322/0.0401	2375 /0.0423	2275 / 0.0322
GOOF on F^2	1.064	1.075	1.089	1.093
R_1, wR_2 (I> 2σ(I))[a]	0.0396, 0.1189	0.0295, 0.0798	0.0250, 0.0480	0.0273, 0.0768
R_1, wR_2 (all data)	0.0444, 0.1276	0.0367, 0.0852	0.0276, 0.0494	0.0407, 0.0836
Absolute structure parameter	0.025(10)	0.018(8)	0.022(9)	0.027(1)
Extinction coefficient	0.0049(6)	0.0028(2)	0.0020(3)	0.0016 (4)
Largest diff. peak and hole (e.Å^{-3})	2.470, -1.552	3.294, -1.347	0.684, -0.703	2.023, -0.628

[a]$R_1 = \Sigma||Fo|—|Fc||/\Sigma|Fo|$, [b]$wR_2 = \Sigma w(F_o^2—F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2a. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $CaMn_6Ga_6S_{16}$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	BVS[a]	Wyckoff	x	y	z	U_{eq}(Å)
Ca(1)	1.6	1b	0	0	5000	26(3)
Ca(2)	1.55	1f	6667	3333	5000	28(3)
Ca(3)	1.57	1d	3333	6667	5000	36(3)
Ga(1)	3.09	6l	4479(2)	3012(2)	2481(3)	14(1)
Ga(2)	2.91	6l	244(1)	2205(2)	2486(3)	12(1)
Ga(3)	3.03	6l	3695(2)	4763(2)	2492(2)	12(1)
Mn(1)	1.91	3j	1407(3)	4285(4)	0	16(1)
Mn(2)	1.93	3k	1394(3)	4192(3)	5000	16(1)
Mn(3)	1.99	3k	6176(4)	5352(3)	5000	17(1)
Mn(4)	1.94	3j	6236(4)	5330(3)	0	18(1)
Mn(5)	2.03	3k	-1990(4)	359(3)	0	17(1)
Mn(6)	2.08	3k	-2006(4)	446(3)	5000	18(1)
S(1)	2.01	3j	717(5)	5375(5)	0	11(2)
S(2)	1.88	3k	1199(6)	2536(6)	5000	11(2)
S(3)	1.87	3k	4113(5)	2072(5)	5000	13(1)
S(4)	1.97	3k	4602(5)	5391(6)	5000	12(2)
S(5)	1.91	3j	4048(5)	2050(5)	0	13(2)
S(6)	1.97	6l	-858(4)	729(4)	2543(6)	12(1)
S(7)	2.14	6l	3235(4)	3235(4)	2498(7)	13(1)
S(8)	1.92	6l	5913(4)	4176(4)	2540(6)	15(1)
S(9)	1.96	3j	1214(6)	2604(7)	0	12(2)
S(10)	1.93	6l	2549(4)	5074(4)	2538(6)	14(1)
S(11)	1.86	6l	39(4)	3449(5)	2505(6)	14(2)

[a]Bond valence state was calculated using the empirical formula $V_i=\Sigma S_{ij}=\Sigma\exp[(r_0-r_{ij})/0.37]$, where S_{ij} is the bond valence associated with bond lengths r_{ij} and r_0。

Table S2b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for $SrMn_6Ga_6S_{16}$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	BVS[a]	Wyckoff	x	y	z	U_{eq}(Å)
Sr(1)	1.78	1e	6667	3333	10000	22(1)
Sr(2)	1.84	1a	0	0	10000	24(1)
Sr(3)	1.82	1c	3333	6667	10000	20(1)
Ga(1)	2.93	6l	5536(1)	6902(1)	7475(2)	10(1)
Ga(2)	2.97	6l	2271(1)	1903(1)	7485(2)	10(1)
Ga(3)	2.92	6l	4794(1)	3643(1)	7467(2)	11(1)
Mn(1)	2.04	3j	3797(2)	4647(2)	10000	16(1)
Mn(2)	2.07	3k	3698(2)	4650(2)	5000	15(1)
Mn(3)	1.98	3j	4134(2)	1298(2)	10000	15(1)
Mn(4)	1.90	3j	561(2)	2501(2)	10000	14(1)
Mn(5)	1.98	3k	4220(2)	1312(2)	5000	13(1)
Mn(6)	1.93	3k	475(2)	2412(2)	5000	14(1)
S(1)	1.89	6l	6774(3)	6709(2)	7505(7)	11(1)
S(2)	2.12	6l	3336(2)	3427(2)	7505(7)	10(1)
S(3)	1.90	3k	5345(4)	4602(3)	5000	11(1)
S(4)	1.80	3j	5390(4)	4570(4)	10000	12(1)
S(5)	2.03	6l	4086(3)	5775(3)	7510(5)	12(1)
S(6)	1.96	6l	5012(3)	2449(3)	7521(5)	12(1)
S(7)	1.90	3j	2508(4)	1245(4)	10000	11(1)
S(8)	1.97	3k	2599(4)	1306(4)	5000	11(1)
S(9)	1.82	3j	5827(4)	7837(4)	10000	11(1)
S(10)	1.95	3k	5909(4)	7865(4)	5000	11(1)
S(11)	1.89	6l	835(3)	1645(3)	7517(4)	12(1)

[a]Bond valence state was calculated using the empirical formula $V_i=\Sigma S_{ij}=\Sigma \exp[(r_0-r_{ij})/0.37]$, where S_{ij} is the bond valence associated with bond lengths r_{ij} and r_0。

Table S2c. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $BaMn_6Ga_6S_{16}$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	BVS[a]	Wyckoff	x	y	z	U_{eq}(Å)
Ba(1)	2.15	1d	3333	6667	5000	18(1)
Ba(2)	2.11	1e	6667	3333	0	16(1)
Ba(3)	2.21	1a	0	0	0	13(1)
Ga(1)	2.90	6l	4485(1)	3032(1)	2521(2)	13(1)
Ga(2)	2.95	6l	3705(1)	4758(1)	2492(2)	12(1)
Ga(3)	2.95	6l	223(1)	2203(1)	2504(2)	12(1)
Mn(1)	1.99	3j	6160(2)	5369(2)	0	12(1)
Mn(2)	1.95	3k	1393(2)	4164(2)	5000	14(1)
Mn(3)	1.91	3j	1378(2)	4201(2)	0	22(1)
Mn(4)	1.98	3k	4615(2)	857(2)	5000	21(1)
Mn(5)	2.03	3j	-2049(2)	450(2)	0	23(1)
Mn(6)	2.07	3k	2414(2)	2034(2)	5000	17(1)
S(1)	1.77	3j	4185(3)	2120(5)	0	12(1)
S(2)	2.07	6l	5863(3)	4255(2)	2516(3)	13(1)
S(3)	1.83	3k	4114(3)	2084(5)	5000	14(1)
S(4)	2.14	6l	3252(2)	3244(2)	2497(10)	12(1)
S(5)	1.79	3k	4596(6)	5433(6)	5000	14(1)
S(6)	1.90	6l	46(2)	3435(2)	2496(10)	12(1)
S(7)	2.09	6l	2494(3)	4945(3)	2488(3)	15(1)
S(8)	1.97	3j	778(3)	5392(6)	0	12(1)
S(9)	1.94	3k	1162(4)	2528(3)	5000	13(1)
S(10)	1.77	3j	1146(4)	2483(3)	0	12(1)
S(11)	2.14	6l	-935(2)	784(3)	2494(3)	14(1)

[a]Bond valence state was calculated using the empirical formula $V_i=\Sigma S_{ij}=\Sigma \exp[(r_0-r_{ij})/0.37]$, where S_{ij} is the bond valence associated with bond lengths r_{ij} and r_0。

Table S2d. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for $PbMn_6Ga_6S_{16}$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	BVS[a]	Wyckoff	x	y	z	U_{eq}(Å)
Pb(1)	1.59	1c	3333	6667	10000	27(1)
Pb(2)	1.66	1a	0	0	10000	29(1)
Pb(3)	1.68	1e	6667	3333	0	26(1)
Ga(1)	2.97	6l	376(1)	2276(1)	7501(4)	13(1)
Ga(2)	2.93	6l	1148(1)	4798(1)	7503(4)	14(1)
Ga(3)	2.95	6l	4465(1)	3089(1)	2499(3)	13(1)
Mn(1)	1.92	3j	-1949(3)	502(3)	10000	20(1)
Mn(2)	1.96	3k	-1947(3)	512(3)	5000	19(1)
Mn(3)	2.03	3k	2872(3)	4170(3)	5000	18(1)
Mn(4)	1.97	3j	2886(3)	4188(3)	10000	18(1)
Mn(5)	2.02	3k	6255(3)	5359(3)	5000	21(1)
Mn(6)	2.12	3j	6274(3)	5361(3)	0	20(1)
S(1)	1.93	6l	-808(2)	831(2)	7496(9)	16(1)
S(2)	1.97	3j	1291(5)	2574(5)	10000	16(2)
S(3)	1.98	3k	1283(5)	2556(5)	5000	14(2)
S(4)	2.16	6l	-92(2)	3335(2)	7533(5)	13(1)
S(5)	1.88	3k	785(6)	5370(5)	5000	17(2)
S(6)	1.87	3j	762(6)	5362(5)	10000	14(2)
S(7)	1.94	6l	2565(2)	5018(2)	7489(8)	16(1)
S(8)	1.91	6l	3230(2)	3292(2)	2532(5)	14(1)
S(9)	1.92	3k	4127(5)	2144(5)	5000	14(2)
S(10)	1.98	3j	4117(5)	2144(5)	0	16(2)
S(11)	1.94	6l	5919(2)	4223(2)	2493(8)	16(1)

[a]Bond valence state was calculated using the empirical formula $V_i=\Sigma S_{ij}=\Sigma \exp[(r_0-r_{ij})/0.37]$, where S_{ij} is the bond valence associated with bond lengths r_{ij} and r_0。

Table S3a. A(I)B_3CQ_8 and M(II)$B_6C_6Q_{16}$ structural data and some optical performances (the red part represents the title compounds).

Compound	cell parameters (Å)	SHG (×AGS)	Eg (eV)	Δn @1064nm	Curie constant / Weiss constant (emu K mol^{-1}/K)
$NaMg_3Ga_3S_8$	a=b=16.7467 c=3.7032	0.3	3.70	0.03@546nm	/
$LiMg_3Ga_3S_8$	a=b=16.6837 c=3.7004	/	3.86	/	/
$NaMg_3Al_3S_8$	a=b=16.7100 c=3.6921	0.4	4.20	0.02@546nm	
$AgMg_3Ga_3S_8$	a=b=16.8433 c=3.7066	0.3	3.59	0.091@546nm	/
$CuMg_3Ga_3S_8$	a=b=16.6442 c=3.6963	/	/	/	/
$AgMg_3Ga_3Se_8$	a=b=17.6600 c=3.8930	/	/	0.17@546nm	/
$LiMg_3Ga_3Se_8$	a=b=17.4769 c=3.8678	/	2.67	/	/
$NaMg_3Ga_3Se_8$	a=b=17.5765 c=3.8811	0.8	2.77	0.079@546nm	
$NaMg_3Al_3Se_8$	a=b=17.5753 c=3.8769	/	/	/	/
$NaMn_3Ga_3S_8$	a=b=16.7891 c=3.7083	1.6	2.50	0.175@2050nm	/
$CaMg_6Ga_6S_{16}$	a=b=16.7006 c=7.3916	0.7	3.54	0.046	/
$SrMg_6Ga_6S_{16}$	a=b=16.8029 c=7.4102	0.8	3.51	0.042	/
$BaMg_6Ga_6S_{16}$	a=b=16.9301 c=7.4225	0.8	3.50	0.041	/
$CaMg_6Ga_6Se_{16}$	a=b=17.5327 c=7.7603	1.6	2.71	0.052	/
$SrMg_6Ga_6Se_{16}$	a=b=17.6115 c=7.7684	1.0	2.71	0.048	/
$BaMg_6Ga_6Se_{16}$	a=b=17.7326 c=7.7899	1.1	2.69	0.044	/
$LaMg_6Ga_6S_{16}$	a=b=16.7006 c=7.3916	0.8	3.00	0.041	/
$CaMn_6Ga_6S_{16}$	a=b=16.7529 c=7.4170	0.4	2.58	0.045	C=4.73 θ=−130.71
$SrMn_6Ga_6S_{16}$	a=b=16.8606 c=7.4237	0.5	2.40	0.046	C=3.97 θ=−125.03
$BaMn_6Ga_6S_{16}$	a=b=16.9986 c=7.4410	0.5	2.55	0.060	C=3.96 θ=−114.09
$PbMn_6Ga_6S_{16}$	a=b=16.8215 c=7.4281	0.7	2.05	0.049	C=4.18 θ=−134.54

Table S3b. Optical properties of compounds $AB_3C_3S_8$ and $MMn_6Ga_6S_{16}$.

Compounds	SHG (×AGS)	Eg (eV)	Δn @1064nm
$NaMg_3Ga_3S_8$	0.3	3.70	0.03@546nm
$LiMg_3Ga_3S_8$	/	3.86	/
$NaMg_3Al_3S_8$	0.4	4.20	0.02@546nm
$AgMg_3Ga_3S_8$	0.3	3.59	0.091@546nm
$CuMg_3Ga_3S_8$	/	/	/
$CaMn_6Ga_6S_{16}$	0.4	2.58	0.045
$SrMn_6Ga_6S_{16}$	0.5	2.40	0.046
$BaMn_6Ga_6S_{16}$	0.5	2.55	0.060
$PbMn_6Ga_6S_{16}$	0.7	2.05	0.049

Table S4a. Selected distances (Å) and angles (degrees) for $CaMn_6Ga_6S_{16}$.

Ca(1)-S(6)#11	2.938(6)	Mn(1)-S(10)	2.534(6)
Ca(1)-S(6)#8	2.938(6)	Mn(1)-S(10)#2	2.534(6)
Ca(1)-S(6)#3	2.938(6)	Mn(1)-S(1)	2.604(8)
Ca(1)-S(6)#10	2.938(6)	Mn(1)-S(9)	2.669(10)
Ca(1)-S(6)#12	2.938(6)	Mn(1)-S(11)#2	2.730(6)
Ca(1)-S(6)	2.939(6)	Mn(1)-S(11)	2.730(6)
Ca(2)-S(8)	2.950(6)	Mn(2)-S(10)#3	2.530(6)
Ca(2)-S(8)#13	2.950(6)	Mn(2)-S(10)	2.530(6)
Ca(2)-S(8)#14	2.950(6)	Mn(2)-S(2)	2.626(10)
Ca(2)-S(8)#6	2.950(6)	Mn(2)-S(4)#4	2.675(9)
Ca(2)-S(8)#15	2.950(6)	Mn(2)-S(11)#3	2.703(6)
Ca(2)-S(8)#3	2.950(6)	Mn(2)-S(11)	2.703(6)
Ca(3)-S(10)#5	2.945(5)	Mn(3)-S(8)#3	2.556(6)
Ca(3)-S(10)#3	2.945(5)	Mn(3)-S(8)	2.556(6)
Ca(3)-S(10)#1	2.945(5)	Mn(3)-S(11)#5	2.612(6)
Ca(3)-S(10)	2.945(5)	Mn(3)-S(11)#1	2.612(6)
Ca(3)-S(10)#16	2.945(5)	Mn(3)-S(3)#6	2.655(8)
Ca(3)-S(10)#4	2.945(5)	Mn(3)-S(4)	2.670(9)
Ga(1)-S(8)	2.212(7)	Mn(4)-S(8)#2	2.556(6)
Ga(1)-S(7)	2.293(5)	Mn(4)-S(8)	2.556(6)
Ga(1)-S(5)	2.312(5)	Mn(4)-S(5)#6	2.598(8)
Ga(1)-S(3)	2.320(5)	Mn(4)-S(11)#1	2.659(6)
Ga(2)-S(6)	2.227(6)	Mn(4)-S(11)#7	2.659(6)
Ga(2)-S(11)	2.275(6)	Mn(4)-S(1)#1	2.709(9)
Ga(2)-S(9)	2.324(5)	Mn(5)-S(6)	2.523(6)
Ga(2)-S(2)	2.336(5)	Mn(5)-S(6)#2	2.523(6)
Ga(3)-S(10)	2.226(7)	Mn(5)-S(9)#8	2.576(7)
Ga(3)-S(7)	2.275(6)	Mn(5)-S(7)#9	2.624(6)
Ga(3)-S(1)#1	2.297(5)	Mn(5)-S(7)#8	2.624(6)
Ga(3)-S(4)	2.297(5)	Mn(5)-S(5)#8	2.797(9)
S(8)-Ga(1)-S(7)	122.1(2)	Mn(6)-S(6)	2.516(7)
S(8)-Ga(1)-S(5)	117.0(2)	Mn(6)-S(6)#3	2.516(7)
S(7)-Ga(1)-S(5)	97.2(2)	Mn(6)-S(7)#8	2.588(6)
S(8)-Ga(1)-S(3)	112.6(2)	Mn(6)-S(7)#10	2.588(6)
S(7)-Ga(1)-S(3)	98.8(2)	Mn(6)-S(2)#8	2.657(8)
S(5)-Ga(1)-S(3)	106.4(3)	Mn(6)-S(3)#8	2.730(9)
S(6)-Ga(2)-S(11)	126.6(3)	S(2)-Mn(2)-S(11)	83.2(2)

S(6)-Ga(2)-S(9)	114.0(3)	S(4)#4-Mn(2)-S(11)	78.4(2)
S(11)-Ga(2)-S(9)	98.4(3)	S(11)#3-Mn(2)-S(11)	86.4(3)
S(6)-Ga(2)-S(2)	109.7(3)	S(10)#3-Mn(2)-Ca(3)	51.13(15)
S(11)-Ga(2)-S(2)	100.2(3)	S(10)-Mn(2)-Ca(3)	51.13(15)
S(9)-Ga(2)-S(2)	105.5(3)	S(2)-Mn(2)-Ca(3)	138.1(2)
S(10)-Ga(3)-S(7)	114.6(2)	S(4)#4-Mn(2)-Ca(3)	67.29(19)
S(10)-Ga(3)-S(1)#1	113.3(2)	S(11)#3-Mn(2)-Ca(3)	124.68(18)
S(7)-Ga(3)-S(1)#1	104.7(2)	S(11)-Mn(2)-Ca(3)	124.68(18)
S(10)-Ga(3)-S(4)	109.3(2)	S(8)#3-Mn(3)-S(8)	91.1(3)
S(7)-Ga(3)-S(4)	106.8(2)	S(8)#3-Mn(3)-S(11)#5	89.22(16)
S(1)#1-Ga(3)-S(4)	107.7(3)	S(8)-Mn(3)-S(11)#5	176.5(3)
S(10)-Mn(1)-S(10)#2	95.9(3)	S(8)#3-Mn(3)-S(11)#1	176.5(3)
S(10)-Mn(1)-S(1)	96.8(2)	S(8)-Mn(3)-S(11)#1	89.22(16)
S(10)#2-Mn(1)-S(1)	96.8(2)	S(11)#5-Mn(3)-S(11)#1	90.2(3)
S(10)-Mn(1)-S(9)	102.2(2)	S(8)#3-Mn(3)-S(3)#6	89.5(3)
S(10)#2-Mn(1)-S(9)	102.2(2)	S(8)-Mn(3)-S(3)#6	89.5(3)
S(1)-Mn(1)-S(9)	151.3(3)	S(11)#5-Mn(3)-S(3)#6	87.05(19)
S(10)-Mn(1)-S(11)#2	173.8(2)	S(11)#1-Mn(3)-S(3)#6	87.05(19)
S(10)#2-Mn(1)-S(11)#2	89.04(18)	S(8)#3-Mn(3)-S(4)	103.1(3)
S(1)-Mn(1)-S(11)#2	78.85(19)	S(8)-Mn(3)-S(4)	103.1(3)
S(9)-Mn(1)-S(11)#2	80.2(2)	S(11)#5-Mn(3)-S(4)	80.1(2)
S(10)-Mn(1)-S(11)	89.05(18)	S(11)#1-Mn(3)-S(4)	80.1(2)
S(10)#2-Mn(1)-S(11)	173.8(2)	S(3)#6-Mn(3)-S(4)	161.8(3)
S(1)-Mn(1)-S(11)	78.85(19)	S(8)#2-Mn(4)-S(8)	95.0(3)
S(9)-Mn(1)-S(11)	80.2(2)	S(8)#2-Mn(4)-S(5)#6	94.1(3)
S(11)#2-Mn(1)-S(11)	85.7(3)	S(8)-Mn(4)-S(5)#6	94.1(3)
S(10)#3-Mn(2)-S(10)	92.4(3)	S(8)#2-Mn(4)-S(11)#1	176.6(3)
S(10)#3-Mn(2)-S(2)	105.8(2)	S(8)-Mn(4)-S(11)#1	88.18(16)
S(10)-Mn(2)-S(2)	105.8(2)	S(5)#6-Mn(4)-S(11)#1	87.00(19)
S(10)#3-Mn(2)-S(4)#4	91.5(2)	S(8)#2-Mn(4)-S(11)#7	88.18(16)
S(10)-Mn(2)-S(4)#4	91.5(2)	S(8)-Mn(4)-S(11)#7	176.6(3)
S(2)-Mn(2)-S(4)#4	154.6(3)	S(5)#6-Mn(4)-S(11)#7	87.00(19)
S(10)#3-Mn(2)-S(11)#3	89.75(18)	S(11)#1-Mn(4)-S(11)#7	88.6(3)
S(10)-Mn(2)-S(11)#3	169.8(2)	S(8)#2-Mn(4)-S(1)#1	99.8(3)
S(2)-Mn(2)-S(11)#3	83.2(2)	S(8)-Mn(4)-S(1)#1	99.8(3)
S(4)#4-Mn(2)-S(11)#3	78.4(2)	S(5)#6-Mn(4)-S(1)#1	159.3(3)
S(10)#3-Mn(2)-S(11)	169.8(2)	S(11)#1-Mn(4)-S(1)#1	78.3(2)
S(10)-Mn(2)-S(11)	89.76(18)	S(11)#7-Mn(4)-S(1)#1	78.3(2)

S(6)-Mn(5)-S(6)#2	96.8(3)	S(6)#3-Ca(1)-S(6)#12	133.81(7)
S(6)-Mn(5)-S(9)#8	95.9(2)	S(6)#10-Ca(1)-S(6)#12	133.81(7)
S(6)#2-Mn(5)-S(9)#8	95.9(2)	S(6)#11-Ca(1)-S(6)	133.81(7)
S(6)-Mn(5)-S(7)#9	176.2(2)	S(6)#8-Ca(1)-S(6)	85.60(15)
S(6)#2-Mn(5)-S(7)#9	86.67(18)	S(6)#3-Ca(1)-S(6)	76.6(2)
S(9)#8-Mn(5)-S(7)#9	85.4(2)	S(6)#10-Ca(1)-S(6)	133.81(7)
S(6)-Mn(5)-S(7)#8	86.67(18)	S(6)#12-Ca(1)-S(6)	85.60(15)
S(6)#2-Mn(5)-S(7)#8	176.2(2)	S(8)-Ca(2)-S(8)#13	133.74(7)
S(9)#8-Mn(5)-S(7)#8	85.4(2)	S(8)-Ca(2)-S(8)#14	85.76(15)
S(7)#9-Mn(5)-S(7)#8	89.8(3)	S(8)#13-Ca(2)-S(8)#14	133.74(7)
S(6)-Mn(5)-S(5)#8	98.6(2)	S(8)-Ca(2)-S(8)#6	85.76(15)
S(6)#2-Mn(5)-S(5)#8	98.6(2)	S(8)#13-Ca(2)-S(8)#6	76.4(2)
S(9)#8-Mn(5)-S(5)#8	158.0(4)	S(8)#14-Ca(2)-S(8)#6	85.76(15)
S(7)#9-Mn(5)-S(5)#8	79.11(19)	S(8)-Ca(2)-S(8)#15	133.74(7)
S(7)#8-Mn(5)-S(5)#8	79.11(19)	S(8)#13-Ca(2)-S(8)#15	85.76(15)
S(6)-Mn(6)-S(6)#3	92.8(3)	S(8)#14-Ca(2)-S(8)#15	76.4(2)
S(6)-Mn(6)-S(7)#8	87.57(18)	S(8)#6-Ca(2)-S(8)#15	133.74(7)
S(6)#3-Mn(6)-S(7)#8	174.9(3)	S(8)-Ca(2)-S(8)#3	76.4(2)
S(6)-Mn(6)-S(7)#10	174.9(3)	S(8)#13-Ca(2)-S(8)#3	85.76(15)
S(6)#3-Mn(6)-S(7)#10	87.57(18)	S(8)#14-Ca(2)-S(8)#3	133.74(7)
S(7)#8-Mn(6)-S(7)#10	91.6(3)	S(8)#6-Ca(2)-S(8)#3	133.74(7)
S(6)-Mn(6)-S(2)#8	90.4(2)	S(8)#15-Ca(2)-S(8)#3	85.76(15)
S(6)#3-Mn(6)-S(2)#8	90.4(2)	S(10)#5-Ca(3)-S(10)#3	85.61(14)
S(7)#8-Mn(6)-S(2)#8	84.6(2)	S(10)#5-Ca(3)-S(10)#1	76.6(2)
S(7)#10-Mn(6)-S(2)#8	84.6(2)	S(10)#3-Ca(3)-S(10)#1	133.81(7)
S(6)-Mn(6)-S(3)#8	102.5(2)	S(10)#5-Ca(3)-S(10)	133.81(7)
S(6)#3-Mn(6)-S(3)#8	102.5(2)	S(10)#3-Ca(3)-S(10)	76.6(2)
S(7)#8-Mn(6)-S(3)#8	82.3(2)	S(10)#1-Ca(3)-S(10)	85.61(14)
S(7)#10-Mn(6)-S(3)#8	82.3(2)	S(10)#5-Ca(3)-S(10)#16	85.61(14)
S(2)#8-Mn(6)-S(3)#8	161.2(4)	S(10)#3-Ca(3)-S(10)#16	85.61(14)
S(6)#11-Ca(1)-S(6)#8	133.81(7)	S(10)#1-Ca(3)-S(10)#16	133.80(7)
S(6)#11-Ca(1)-S(6)#3	85.60(15)	S(10)-Ca(3)-S(10)#16	133.80(7)
S(6)#8-Ca(1)-S(6)#3	133.81(7)	S(10)#5-Ca(3)-S(10)#4	133.80(7)
S(6)#11-Ca(1)-S(6)#10	85.60(15)	S(10)#3-Ca(3)-S(10)#4	133.80(7)
S(6)#8-Ca(1)-S(6)#10	76.6(2)	S(10)#1-Ca(3)-S(10)#4	85.61(14)
S(6)#3-Ca(1)-S(6)#10	85.60(15)	S(10)-Ca(3)-S(10)#4	85.61(14)
S(6)#11-Ca(1)-S(6)#12	76.6(2)	S(10)#16-Ca(3)-S(10)#4	76.6(2)
S(6)#8-Ca(1)-S(6)#12	85.60(15)		

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,x-y+1,z #2 x,y,-z #3 x,y,-z+1 #4 -x+y,-x+1,z

#5 -y+1,x-y+1,-z+1 #6 -x+y+1,-x+1,z #7 -y+1,x-y+1,-z

#8 -y,x-y,z #9 -y,x-y,-z #10 -y,x-y,-z+1

#11 -x+y,-x,-z+1 #12 -x+y,-x,z #13 -x+y+1,-x+1,-z+1

#14 -y+1,x-y,z #15 -y+1,x-y,-z+1 #16 -x+y,-x+1,-z+1

#17 -x+y,-x+1,-z

Table S4b. Selected distances (Å) and angles (degrees) for SrMn6Ga6S16.

Sr(1)-S(6)#1	3.039(4)	Ga(3)-S(3)	2.308(4)
Sr(1)-S(6)#2	3.039(4)	Ga(3)-S(4)	2.327(4)
Sr(1)-S(6)	3.039(4)	Mn(1)-S(5)#4	2.518(5)
Sr(1)-S(6)#3	3.039(4)	Mn(1)-S(5)	2.518(5)
Sr(1)-S(6)#4	3.039(4)	Mn(1)-S(2)#4	2.582(5)
Sr(1)-S(6)#5	3.039(4)	Mn(1)-S(2)	2.582(5)
Sr(1)-S(4)#2	3.669(6)	Mn(1)-S(9)#10	2.703(6)
Sr(1)-S(4)#5	3.669(6)	Mn(1)-S(4)	2.755(7)
Sr(1)-S(4)	3.669(6)	Mn(2)-S(5)#14	2.501(4)
Sr(2)-S(11)	3.028(4)	Mn(2)-S(5)	2.501(4)
Sr(2)-S(11)#4	3.028(4)	Mn(2)-S(10)#10	2.598(6)
Sr(2)-S(11)#6	3.028(4)	Mn(2)-S(2)	2.611(5)
Sr(2)-S(11)#7	3.028(4)	Mn(2)-S(2)#14	2.611(5)
Sr(2)-S(11)#8	3.028(4)	Mn(2)-S(3)	2.818(7)
Sr(2)-S(11)#9	3.028(4)	Mn(3)-S(6)#4	2.544(4)
Sr(2)-S(7)	3.662(5)	Mn(3)-S(6)	2.544(4)
Sr(2)-S(7)#8	3.662(5)	Mn(3)-S(1)#2	2.611(5)
Sr(2)-S(7)#6	3.662(5)	Mn(3)-S(1)#1	2.611(5)
Sr(3)-S(5)	3.032(4)	Mn(3)-S(4)#2	2.679(6)
Sr(3)-S(5)#10	3.032(4)	Mn(3)-S(7)	2.699(6)
Sr(3)-S(5)#11	3.032(4)	Mn(4)-S(11)	2.522(4)
Sr(3)-S(5)#12	3.032(4)	Mn(4)-S(11)#4	2.522(4)
Sr(3)-S(5)#13	3.032(4)	Mn(4)-S(9)#10	2.651(6)
Sr(3)-S(5)#4	3.032(4)	Mn(4)-S(7)#6	2.697(6)
Sr(3)-S(9)	3.644(5)	Mn(4)-S(1)#12	2.707(5)
Sr(3)-S(9)#13	3.644(5)	Mn(4)-S(1)#10	2.707(5)
Sr(3)-S(9)#10	3.644(5)	Mn(5)-S(6)#14	2.531(4)
Ga(1)-S(5)	2.224(4)	Mn(5)-S(6)	2.531(4)
Ga(1)-S(1)	2.269(4)	Mn(5)-S(3)#2	2.602(6)
Ga(1)-S(10)	2.321(4)	Mn(5)-S(1)#15	2.653(5)
Ga(1)-S(9)	2.338(3)	Mn(5)-S(1)#2	2.653(5)
Ga(2)-S(11)	2.235(4)	Mn(5)-S(8)	2.728(6)
Ga(2)-S(2)	2.284(4)	Mn(6)-S(11)	2.514(4)
Ga(2)-S(8)	2.298(3)	Mn(6)-S(11)#14	2.514(4)
Ga(2)-S(7)	2.306(3)	Mn(6)-S(8)#6	2.628(6)
Ga(3)-S(6)	2.219(4)	Mn(6)-S(10)#10	2.680(6)
Ga(3)-S(2)	2.299(3)	Mn(6)-S(1)#10	2.723(5)

Mn(6)-S(1)#16	2.723(5)	S(11)-Sr(2)-S(11)#6	86.80(10)
S(6)#1-Sr(1)-S(6)#2	74.55(14)	S(11)#4-Sr(2)-S(11)#6	133.26(5)
S(6)#1-Sr(1)-S(6)	133.11(5)	S(11)-Sr(2)-S(11)#7	133.26(5)
S(6)#2-Sr(1)-S(6)	87.12(10)	S(11)#4-Sr(2)-S(11)#7	86.80(10)
S(6)#1-Sr(1)-S(6)#3	87.12(10)	S(11)#6-Sr(2)-S(11)#7	133.26(5)
S(6)#2-Sr(1)-S(6)#3	133.11(5)	S(11)-Sr(2)-S(11)#8	86.80(10)
S(6)-Sr(1)-S(6)#3	133.11(5)	S(11)#4-Sr(2)-S(11)#8	133.26(5)
S(6)#1-Sr(1)-S(6)#4	87.12(10)	S(11)#6-Sr(2)-S(11)#8	86.80(10)
S(6)#2-Sr(1)-S(6)#4	133.11(5)	S(11)#7-Sr(2)-S(11)#8	75.00(14)
S(6)-Sr(1)-S(6)#4	74.55(14)	S(11)-Sr(2)-S(11)#9	133.26(5)
S(6)#3-Sr(1)-S(6)#4	87.12(10)	S(11)#4-Sr(2)-S(11)#9	86.80(10)
S(6)#1-Sr(1)-S(6)#5	133.11(5)	S(11)#6-Sr(2)-S(11)#9	75.00(14)
S(6)#2-Sr(1)-S(6)#5	87.12(10)	S(11)#7-Sr(2)-S(11)#9	86.80(10)
S(6)-Sr(1)-S(6)#5	87.12(10)	S(11)#8-Sr(2)-S(11)#9	133.26(5)
S(6)#3-Sr(1)-S(6)#5	74.55(14)	S(11)-Sr(2)-S(7)	66.42(10)
S(6)#4-Sr(1)-S(6)#5	133.11(5)	S(11)#4-Sr(2)-S(7)	66.42(10)
S(6)#1-Sr(1)-S(4)#2	67.87(9)	S(11)#6-Sr(2)-S(7)	142.50(7)
S(6)#2-Sr(1)-S(4)#2	67.87(9)	S(11)#7-Sr(2)-S(7)	66.84(10)
S(6)-Sr(1)-S(4)#2	65.26(9)	S(11)#8-Sr(2)-S(7)	66.84(10)
S(6)#3-Sr(1)-S(4)#2	142.69(7)	S(11)#9-Sr(2)-S(7)	142.50(7)
S(6)#4-Sr(1)-S(4)#2	65.26(9)	S(11)-Sr(2)-S(7)#8	142.50(7)
S(6)#5-Sr(1)-S(4)#2	142.69(7)	S(11)#4-Sr(2)-S(7)#8	142.50(7)
S(6)#1-Sr(1)-S(4)#5	65.26(9)	S(11)#6-Sr(2)-S(7)#8	66.84(10)
S(6)#2-Sr(1)-S(4)#5	65.26(10)	S(11)#7-Sr(2)-S(7)#8	66.42(10)
S(6)-Sr(1)-S(4)#5	142.69(7)	S(11)#8-Sr(2)-S(7)#8	66.42(10)
S(6)#3-Sr(1)-S(4)#5	67.86(9)	S(11)#9-Sr(2)-S(7)#8	66.84(10)
S(6)#4-Sr(1)-S(4)#5	142.69(7)	S(7)-Sr(2)-S(7)#8	120
S(6)#5-Sr(1)-S(4)#5	67.86(9)	S(11)-Sr(2)-S(7)#6	66.84(10)
S(4)#2-Sr(1)-S(4)#5	120	S(11)#4-Sr(2)-S(7)#6	66.84(10)
S(6)#1-Sr(1)-S(4)	142.69(7)	S(11)#6-Sr(2)-S(7)#6	66.42(10)
S(6)#2-Sr(1)-S(4)	142.69(7)	S(11)#7-Sr(2)-S(7)#6	142.50(7)
S(6)-Sr(1)-S(4)	67.86(9)	S(11)#8-Sr(2)-S(7)#6	142.50(7)
S(6)#3-Sr(1)-S(4)	65.26(9)	S(11)#9-Sr(2)-S(7)#6	66.42(10)
S(6)#4-Sr(1)-S(4)	67.86(9)	S(7)-Sr(2)-S(7)#6	120.000(1)
S(6)#5-Sr(1)-S(4)	65.26(9)	S(7)#8-Sr(2)-S(7)#6	120.000(1)
S(4)#2-Sr(1)-S(4)	119.999(1)	S(5)-Sr(3)-S(5)#10	86.72(11)
S(4)#5-Sr(1)-S(4)	119.999(1)	S(5)-Sr(3)-S(5)#11	133.29(5)
S(11)-Sr(2)-S(11)#4	75.00(14)	S(5)#10-Sr(3)-S(5)#11	133.29(5)

$S(5)-Sr(3)-S(5)^{\#}12$	133.29(5)	S(10)-Ga(1)-S(9)	105.72(17)
$S(5)^{\#}10-Sr(3)-S(5)^{\#}12$	75.11(15)	S(11)-Ga(2)-S(2)	112.62(14)
$S(5)^{\#}11-Sr(3)-S(5)^{\#}12$	86.72(11)	S(11)-Ga(2)-S(8)	113.44(17)
$S(5)-Sr(3)-S(5)^{\#}13$	86.72(11)	S(2)-Ga(2)-S(8)	105.79(18)
$S(5)^{\#}10-Sr(3)-S(5)^{\#}13$	86.72(11)	S(11)-Ga(2)-S(7)	109.23(17)
$S(5)^{\#}11-Sr(3)-S(5)^{\#}13$	75.11(15)	S(2)-Ga(2)-S(7)	107.96(19)
$S(5)^{\#}12-Sr(3)-S(5)^{\#}13$	133.29(5)	S(8)-Ga(2)-S(7)	107.53(17)
$S(5)-Sr(3)-S(5)^{\#}4$	75.11(15)	S(6)-Ga(3)-S(2)	120.35(15)
$S(5)^{\#}10-Sr(3)-S(5)^{\#}4$	133.29(5)	S(6)-Ga(3)-S(3)	117.26(17)
$S(5)^{\#}11-Sr(3)-S(5)^{\#}4$	86.72(11)	S(2)-Ga(3)-S(3)	98.31(19)
$S(5)^{\#}12-Sr(3)-S(5)^{\#}4$	86.72(11)	S(6)-Ga(3)-S(4)	112.49(17)
$S(5)^{\#}13-Sr(3)-S(5)^{\#}4$	133.29(5)	S(2)-Ga(3)-S(4)	99.51(19)
S(5)-Sr(3)-S(9)	67.24(10)	S(3)-Ga(3)-S(4)	106.47(17)
$S(5)^{\#}10-Sr(3)-S(9)$	142.44(7)	$S(5)^{\#}4-Mn(1)-S(5)$	94.4(2)
$S(5)^{\#}11-Sr(3)-S(9)$	66.06(10)	$S(5)^{\#}4-Mn(1)-S(2)^{\#}4$	86.69(13)
$S(5)^{\#}12-Sr(3)-S(9)$	142.44(7)	$S(5)-Mn(1)-S(2)^{\#}4$	174.52(19)
$S(5)^{\#}13-Sr(3)-S(9)$	66.06(10)	$S(5)^{\#}4-Mn(1)-S(2)$	174.52(19)
$S(5)^{\#}4-Sr(3)-S(9)$	67.24(10)	S(5)-Mn(1)-S(2)	86.69(13)
$S(5)-Sr(3)-S(9)^{\#}13$	142.44(7)	$S(2)^{\#}4-Mn(1)-S(2)$	91.7(2)
$S(5)^{\#}10-Sr(3)-S(9)^{\#}13$	66.06(10)	$S(5)^{\#}4-Mn(1)-S(9)^{\#}10$	89.41(15)
$S(5)^{\#}11-Sr(3)-S(9)^{\#}13$	67.24(10)	$S(5)-Mn(1)-S(9)^{\#}10$	89.41(15)
$S(5)^{\#}12-Sr(3)-S(9)^{\#}13$	66.06(10)	$S(2)^{\#}4-Mn(1)-S(9)^{\#}10$	85.24(14)
$S(5)^{\#}13-Sr(3)-S(9)^{\#}13$	67.24(10)	$S(2)-Mn(1)-S(9)^{\#}10$	85.24(14)
$S(5)^{\#}4-Sr(3)-S(9)^{\#}13$	142.44(7)	$S(5)^{\#}4-Mn(1)-S(4)$	102.17(15)
$S(9)-Sr(3)-S(9)^{\#}13$	120.000(1)	S(5)-Mn(1)-S(4)	102.17(15)
$S(5)-Sr(3)-S(9)^{\#}10$	66.06(10)	$S(2)^{\#}4-Mn(1)-S(4)$	82.80(13)
$S(5)^{\#}10-Sr(3)-S(9)^{\#}10$	67.24(10)	S(2)-Mn(1)-S(4)	82.80(13)
$S(5)^{\#}11-Sr(3)-S(9)^{\#}10$	142.44(7)	$S(9)^{\#}10-Mn(1)-S(4)$	162.8(2)
$S(5)^{\#}12-Sr(3)-S(9)^{\#}10$	67.24(10)	$S(5)^{\#}14-Mn(2)-S(5)$	96.3(2)
$S(5)^{\#}13-Sr(3)-S(9)^{\#}10$	142.44(7)	$S(5)^{\#}14-Mn(2)-S(10)^{\#}10$	95.42(15)
$S(5)^{\#}4-Sr(3)-S(9)^{\#}10$	66.06(10)	$S(5)-Mn(2)-S(10)^{\#}10$	95.42(15)
$S(9)-Sr(3)-S(9)^{\#}10$	120	$S(5)^{\#}14-Mn(2)-S(2)$	176.55(18)
$S(9)^{\#}13-Sr(3)-S(9)^{\#}10$	120	S(5)-Mn(2)-S(2)	86.40(13)
S(5)-Ga(1)-S(1)	125.08(16)	$S(10)^{\#}10-Mn(2)-S(2)$	86.43(14)
S(5)-Ga(1)-S(10)	113.89(18)	$S(5)^{\#}14-Mn(2)-S(2)^{\#}14$	86.40(13)
S(1)-Ga(1)-S(10)	99.3(2)	$S(5)-Mn(2)-S(2)^{\#}14$	176.55(18)
S(5)-Ga(1)-S(9)	109.74(18)	$S(10)^{\#}10-Mn(2)-S(2)^{\#}14$	86.43(14)
S(1)-Ga(1)-S(9)	101.00(19)	$S(2)-Mn(2)-S(2)^{\#}14$	90.8(2)

S(5)#14-Mn(2)-S(3)	97.71(15)	S(7)#6-Mn(4)-S(1)#10	78.78(13)
S(5)-Mn(2)-S(3)	97.71(15)	S(1)#12-Mn(4)-S(1)#10	86.4(2)
S(10)#10-Mn(2)-S(3)	160.3(2)	S(11)-Mn(4)-Sr(2)	52.09(11)
S(2)-Mn(2)-S(3)	79.77(12)	S(6)#14-Mn(5)-S(3)#2	93.92(16)
S(2)#14-Mn(2)-S(3)	79.77(12)	S(6)-Mn(5)-S(3)#2	93.92(16)
S(6)#4-Mn(3)-S(6)	92.7(2)	S(6)#14-Mn(5)-S(1)#15	87.77(13)
S(6)#4-Mn(3)-S(1)#2	176.45(19)	S(6)-Mn(5)-S(1)#15	176.18(19)
S(6)-Mn(3)-S(1)#2	88.39(13)	S(3)#2-Mn(5)-S(1)#15	88.03(15)
S(6)#4-Mn(3)-S(1)#1	88.39(13)	S(6)#14-Mn(5)-S(1)#2	176.18(19)
S(6)-Mn(3)-S(1)#1	176.45(19)	S(6)-Mn(5)-S(1)#2	87.77(13)
S(1)#2-Mn(3)-S(1)#1	90.4(2)	S(3)#2-Mn(5)-S(1)#2	88.03(15)
S(6)#4-Mn(3)-S(4)#2	88.78(16)	S(1)#15-Mn(5)-S(1)#2	89.0(2)
S(6)-Mn(3)-S(4)#2	88.78(16)	S(6)#14-Mn(5)-S(8)	98.67(15)
S(1)#2-Mn(3)-S(4)#2	87.85(15)	S(6)-Mn(5)-S(8)	98.67(15)
S(1)#1-Mn(3)-S(4)#2	87.85(15)	S(3)#2-Mn(5)-S(8)	161.2(2)
S(6)#4-Mn(3)-S(7)	102.64(15)	S(1)#15-Mn(5)-S(8)	78.66(14)
S(6)-Mn(3)-S(7)	102.64(15)	S(1)#2-Mn(5)-S(8)	78.66(14)
S(1)#2-Mn(3)-S(7)	80.42(15)	S(11)-Mn(6)-S(11)#14	96.0(2)
S(1)#1-Mn(3)-S(7)	80.42(15)	S(11)-Mn(6)-S(8)#6	96.55(15)
S(4)#2-Mn(3)-S(7)	163.3(2)	S(11)#14-Mn(6)-S(8)#6	96.55(15)
S(11)-Mn(4)-S(11)#4	93.9(2)	S(11)-Mn(6)-S(10)#10	101.88(16)
S(11)-Mn(4)-S(9)#10	105.83(15)	S(11)#14-Mn(6)-S(10)#10	101.88(16)
S(11)#4-Mn(4)-S(9)#10	105.83(15)	S(8)#6-Mn(6)-S(10)#10	152.3(2)
S(11)-Mn(4)-S(7)#6	90.94(15)	S(11)-Mn(6)-S(1)#10	88.81(14)
S(11)#4-Mn(4)-S(7)#6	90.94(15)	S(11)#14-Mn(6)-S(1)#10	173.91(16)
S(9)#10-Mn(4)-S(7)#6	155.1(2)	S(8)#6-Mn(6)-S(1)#10	79.17(13)
S(11)-Mn(4)-S(1)#12	169.37(18)	S(10)#10-Mn(6)-S(1)#10	80.66(14)
S(11)#4-Mn(4)-S(1)#12	89.00(14)	S(11)-Mn(6)-S(1)#16	173.91(16)
S(9)#10-Mn(4)-S(1)#12	83.12(14)	S(11)#14-Mn(6)-S(1)#16	88.81(14)
S(7)#6-Mn(4)-S(1)#12	78.78(13)	S(8)#6-Mn(6)-S(1)#16	79.17(13)
S(11)-Mn(4)-S(1)#10	89.00(14)	S(10)#10-Mn(6)-S(1)#16	80.66(14)
S(11)#4-Mn(4)-S(1)#10	169.37(18)	S(1)#10-Mn(6)-S(1)#16	86.1(2)
S(9)#10-Mn(4)-S(1)#10	83.12(14)		

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,x-y,-z+2 #2 -y+1,x-y,z #3 -x+y+1,-x+1,-z+2

#4 x,y,-z+2 #5 -x+y+1,-x+1,z #6 -y,x-y,z

#7 -x+y,-x,-z+2 #8 -x+y,-x,z #9 -y,x-y,-z+2

#10 -x+y,-x+1,z #11 -y+1,x-y+1,-z+2 #12 -x+y,-x+1,-z+2

#13 -y+1,x-y+1,z #14 x,y,-z+1 #15 -y+1,x-y,-z+1
#16 -x+y,-x+1,-z+1

Table S4c. Selected distances (Å) and angles (degrees) for BaMn6Ga6S16.

Ba(1)-S(7)	3.149(4)	Ba(3)-S(10)#16	3.659(5)
Ba(1)-S(7)#1	3.149(4)	Ba(3)-S(10)	3.659(5)
Ba(1)-S(7)#2	3.149(4)	Ba(3A)-S(2)#21	3.143(3)
Ba(1)-S(7)#3	3.149(4)	Ba(3A)-S(2)#13	3.143(3)
Ba(1)-S(7)#4	3.149(4)	Ba(3A)-S(2)#10	3.143(3)
Ba(1)-S(7)#5	3.149(4)	Ba(3A)-S(2)#22	3.143(3)
Ba(1)-S(5)#2	3.675(5)	Ba(3A)-S(2)	3.143(3)
Ba(1)-S(5)#4	3.675(5)	Ba(3A)-S(2)#5	3.143(3)
Ba(1)-S(5)	3.675(5)	Ga(1)-S(2)	2.223(4)
Ba(1A)-S(7)	3.139(4)	Ga(1)-S(4)	2.298(3)
Ba(1A)-S(7)#7	3.139(4)	Ga(1)-S(3)	2.320(5)
Ba(1A)-S(7)#2	3.139(4)	Ga(1)-S(1)	2.322(5)
Ba(1A)-S(7)#4	3.139(4)	Ga(2)-S(7)	2.234(4)
Ba(1A)-S(7)#8	3.139(4)	Ga(2)-S(4)	2.287(3)
Ba(1A)-S(7)#9	3.139(4)	Ga(2)-S(8)#4	2.301(5)
Ba(2)-S(2)	3.157(3)	Ga(2)-S(5)	2.314(6)
Ba(2)-S(2)#10	3.157(3)	Ga(3)-S(11)	2.225(4)
Ba(2)-S(2)#11	3.157(3)	Ga(3)-S(6)	2.260(4)
Ba(2)-S(2)#12	3.157(3)	Ga(3)-S(10)	2.326(4)
Ba(2)-S(2)#13	3.157(3)	Ga(3)-S(9)	2.328(4)
Ba(2)-S(2)#8	3.157(3)	Mn(1)-S(2)#8	2.527(3)
Ba(2)-S(1)#13	3.654(4)	Mn(1)-S(2)	2.527(3)
Ba(2)-S(1)	3.654(4)	Mn(1)-S(6)#4	2.632(6)
Ba(2)-S(1)#10	3.654(4)	Mn(1)-S(6)#9	2.632(6)
Ba(2A)-S(11)#5	3.146(3)	Mn(1)-S(8)#4	2.653(7)
Ba(2A)-S(11)	3.146(3)	Mn(1)-S(1)#10	2.719(9)
Ba(2A)-S(11)#15	3.146(3)	Mn(2)-S(7)#5	2.505(4)
Ba(2A)-S(11)#16	3.146(3)	Mn(2)-S(7)	2.505(4)
Ba(2A)-S(11)#17	3.146(3)	Mn(2)-S(9)	2.607(5)
Ba(2A)-S(11)#18	3.146(3)	Mn(2)-S(5)#2	2.707(10)
Ba(3)-S(11)#8	3.140(3)	Mn(2)-S(6)#5	2.723(6)
Ba(3)-S(11)	3.140(3)	Mn(2)-S(6)	2.723(6)
Ba(3)-S(11)#16	3.140(3)	Mn(3)-S(7)	2.495(4)
Ba(3)-S(11)#19	3.140(3)	Mn(3)-S(7)#8	2.495(4)
Ba(3)-S(11)#20	3.140(3)	Mn(3)-S(8)	2.685(10)
Ba(3)-S(11)#17	3.140(3)	Mn(3)-S(6)#8	2.707(6)
Ba(3)-S(10)#17	3.659(5)	Mn(3)-S(6)	2.707(6)

Mn(3)-S(10)	2.744(6)	S(7)#4-Ba(1)-S(5)#2	143.60(6)
Mn(4)-S(2)#22	2.506(3)	S(7)#5-Ba(1)-S(5)#2	66.61(13)
Mn(4)-S(2)#13	2.506(3)	S(7)-Ba(1)-S(5)#4	143.60(6)
Mn(4)-S(3)	2.617(9)	S(7)#1-Ba(1)-S(5)#4	66.61(13)
Mn(4)-S(6)#16	2.640(6)	S(7)#2-Ba(1)-S(5)#4	66.61(13)
Mn(4)-S(6)#15	2.640(6)	S(7)#3-Ba(1)-S(5)#4	65.93(13)
Mn(4)-S(5)#13	2.840(7)	S(7)#4-Ba(1)-S(5)#4	65.93(13)
Mn(5)-S(11)	2.505(4)	S(7)#5-Ba(1)-S(5)#4	143.60(6)
Mn(5)-S(11)#8	2.505(4)	S(5)#2-Ba(1)-S(5)#4	120
Mn(5)-S(4)#20	2.573(6)	S(7)-Ba(1)-S(5)	65.93(13)
Mn(5)-S(4)#17	2.573(6)	S(7)#1-Ba(1)-S(5)	143.60(6)
Mn(5)-S(10)#17	2.744(7)	S(7)#2-Ba(1)-S(5)	143.60(6)
Mn(5)-S(1)#17	2.808(6)	S(7)#3-Ba(1)-S(5)	66.61(13)
Mn(6)-S(11)#16	2.481(4)	S(7)#4-Ba(1)-S(5)	66.61(13)
Mn(6)-S(11)#15	2.481(4)	S(7)#5-Ba(1)-S(5)	65.93(13)
Mn(6)-S(4)	2.608(6)	S(5)#2-Ba(1)-S(5)	120.000(1)
Mn(6)-S(4)#5	2.608(6)	S(5)#4-Ba(1)-S(5)	120.000(2)
Mn(6)-S(9)	2.649(6)	S(7)-Ba(1A)-S(7)#7	132.37(4)
Mn(6)-S(3)	2.849(6)	S(7)-Ba(1A)-S(7)#2	88.75(8)
S(7)-Ba(1)-S(7)#1	132.54(4)	S(7)#7-Ba(1A)-S(7)#2	72.29(11)
S(7)-Ba(1)-S(7)#2	88.39(8)	S(7)-Ba(1A)-S(7)#4	88.75(8)
S(7)#1-Ba(1)-S(7)#2	72.80(11)	S(7)#7-Ba(1A)-S(7)#4	132.37(4)
S(7)-Ba(1)-S(7)#3	132.54(4)	S(7)#2-Ba(1A)-S(7)#4	88.75(8)
S(7)#1-Ba(1)-S(7)#3	88.39(8)	S(7)-Ba(1A)-S(7)#8	72.29(11)
S(7)#2-Ba(1)-S(7)#3	132.54(4)	S(7)#7-Ba(1A)-S(7)#8	88.75(8)
S(7)-Ba(1)-S(7)#4	88.39(8)	S(7)#2-Ba(1A)-S(7)#8	132.37(4)
S(7)#1-Ba(1)-S(7)#4	132.54(4)	S(7)#4-Ba(1A)-S(7)#8	132.37(4)
S(7)#2-Ba(1)-S(7)#4	88.39(8)	S(7)-Ba(1A)-S(7)#9	132.37(4)
S(7)#3-Ba(1)-S(7)#4	72.80(11)	S(7)#7-Ba(1A)-S(7)#9	88.75(8)
S(7)-Ba(1)-S(7)#5	72.80(11)	S(7)#2-Ba(1A)-S(7)#9	132.37(4)
S(7)#1-Ba(1)-S(7)#5	88.39(8)	S(7)#4-Ba(1A)-S(7)#9	72.29(11)
S(7)#2-Ba(1)-S(7)#5	132.54(4)	S(7)#8-Ba(1A)-S(7)#9	88.75(8)
S(7)#3-Ba(1)-S(7)#5	88.39(8)	S(2)-Ba(2)-S(2)#10	88.42(8)
S(7)#4-Ba(1)-S(7)#5	132.54(4)	S(2)-Ba(2)-S(2)#11	132.52(3)
S(7)-Ba(1)-S(5)#2	66.61(13)	S(2)#10-Ba(2)-S(2)#11	132.52(3)
S(7)#1-Ba(1)-S(5)#2	65.93(13)	S(2)-Ba(2)-S(2)#12	132.52(3)
S(7)#2-Ba(1)-S(5)#2	65.93(13)	S(2)#10-Ba(2)-S(2)#12	72.75(11)
S(7)#3-Ba(1)-S(5)#2	143.60(6)	S(2)#11-Ba(2)-S(2)#12	88.42(8)

S(2)-Ba(2)-S(2)#13	88.42(8)	S(11)#15-Ba(2A)-S(11)#17	132.51(3)
S(2)#10-Ba(2)-S(2)#13	88.42(8)	S(11)#16-Ba(2A)-S(11)#17	88.44(7)
S(2)#11-Ba(2)-S(2)#13	72.75(11)	S(11)#5-Ba(2A)-S(11)#18	88.45(7)
S(2)#12-Ba(2)-S(2)#13	132.52(3)	S(11)-Ba(2A)-S(11)#18	132.51(3)
S(2)-Ba(2)-S(2)#8	72.75(11)	S(11)#15-Ba(2A)-S(11)#18	88.44(7)
S(2)#10-Ba(2)-S(2)#8	132.52(3)	S(11)#16-Ba(2A)-S(11)#18	132.51(3)
S(2)#11-Ba(2)-S(2)#8	88.42(8)	S(11)#17-Ba(2A)-S(11)#18	72.71(10)
S(2)#12-Ba(2)-S(2)#8	88.42(8)	S(11)#8-Ba(3)-S(11)	72.44(11)
S(2)#13-Ba(2)-S(2)#8	132.52(3)	S(11)#8-Ba(3)-S(11)#16	132.42(3)
S(2)-Ba(2)-S(1)#13	143.60(5)	S(11)-Ba(3)-S(11)#16	88.64(8)
S(2)#10-Ba(2)-S(1)#13	65.09(12)	S(11)#8-Ba(3)-S(11)#19	88.64(8)
S(2)#11-Ba(2)-S(1)#13	67.44(12)	S(11)-Ba(3)-S(11)#19	132.42(3)
S(2)#12-Ba(2)-S(1)#13	65.09(12)	S(11)#16-Ba(3)-S(11)#19	72.44(11)
S(2)#13-Ba(2)-S(1)#13	67.44(12)	S(11)#8-Ba(3)-S(11)#20	88.64(8)
S(2)#8-Ba(2)-S(1)#13	143.60(5)	S(11)-Ba(3)-S(11)#20	132.42(3)
S(2)-Ba(2)-S(1)	67.44(12)	S(11)#16-Ba(3)-S(11)#20	132.42(3)
S(2)#10-Ba(2)-S(1)	143.60(5)	S(11)#19-Ba(3)-S(11)#20	88.64(8)
S(2)#11-Ba(2)-S(1)	65.09(12)	S(11)#8-Ba(3)-S(11)#17	132.42(3)
S(2)#12-Ba(2)-S(1)	143.60(5)	S(11)-Ba(3)-S(11)#17	88.64(8)
S(2)#13-Ba(2)-S(1)	65.09(12)	S(11)#16-Ba(3)-S(11)#17	88.64(8)
S(2)#8-Ba(2)-S(1)	67.44(12)	S(11)#19-Ba(3)-S(11)#17	132.42(3)
S(1)#13-Ba(2)-S(1)	120.000(1)	S(11)#20-Ba(3)-S(11)#17	72.44(11)
S(2)-Ba(2)-S(1)#10	65.09(12)	S(11)#8-Ba(3)-S(10)#17	65.93(10)
S(2)#10-Ba(2)-S(1)#10	67.44(12)	S(11)-Ba(3)-S(10)#17	65.93(10)
S(2)#11-Ba(2)-S(1)#10	143.60(5)	S(11)#16-Ba(3)-S(10)#17	143.78(5)
S(2)#12-Ba(2)-S(1)#10	67.44(12)	S(11)#19-Ba(3)-S(10)#17	143.78(5)
S(2)#13-Ba(2)-S(1)#10	143.60(5)	S(11)#20-Ba(3)-S(10)#17	66.49(10)
S(2)#8-Ba(2)-S(1)#10	65.09(12)	S(11)#17-Ba(3)-S(10)#17	66.49(10)
S(1)#13-Ba(2)-S(1)#10	120	S(11)#8-Ba(3)-S(10)#16	143.78(5)
S(1)-Ba(2)-S(1)#10	120	S(11)-Ba(3)-S(10)#16	143.78(5)
S(11)#5-Ba(2A)-S(11)	72.71(10)	S(11)#16-Ba(3)-S(10)#16	66.49(10)
S(11)#5-Ba(2A)-S(11)#15	88.45(7)	S(11)#19-Ba(3)-S(10)#16	66.49(10)
S(11)-Ba(2A)-S(11)#15	132.51(3)	S(11)#20-Ba(3)-S(10)#16	65.93(10)
S(11)#5-Ba(2A)-S(11)#16	132.51(3)	S(11)#17-Ba(3)-S(10)#16	65.93(10)
S(11)-Ba(2A)-S(11)#16	88.45(7)	S(10)#17-Ba(3)-S(10)#16	120
S(11)#15-Ba(2A)-S(11)#16	72.71(10)	S(11)#8-Ba(3)-S(10)	66.49(10)
S(11)#5-Ba(2A)-S(11)#17	132.51(3)	S(11)-Ba(3)-S(10)	66.49(10)
S(11)-Ba(2A)-S(11)#17	88.45(7)	S(11)#16-Ba(3)-S(10)	65.93(10)

S(11)#19-Ba(3)-S(10)	65.93(10)	S(2)#8-Mn(1)-S(2)	95.58(16)
S(11)#20-Ba(3)-S(10)	143.78(5)	S(2)#8-Mn(1)-S(6)#4	176.12(17)
S(11)#17-Ba(3)-S(10)	143.78(5)	S(2)-Mn(1)-S(6)#4	87.26(14)
S(10)#17-Ba(3)-S(10)	120	S(2)#8-Mn(1)-S(6)#9	87.26(14)
S(10)#16-Ba(3)-S(10)	120	S(2)-Mn(1)-S(6)#9	176.12(17)
S(2)#21-Ba(3A)-S(2)#13	132.29(3)	S(6)#4-Mn(1)-S(6)#9	89.8(3)
S(2)#21-Ba(3A)-S(2)#10	72.05(11)	S(2)#8-Mn(1)-S(8)#4	100.44(17)
S(2)#13-Ba(3A)-S(2)#10	88.92(8)	S(2)-Mn(1)-S(8)#4	100.44(17)
S(2)#21-Ba(3A)-S(2)#22	88.92(8)	S(6)#4-Mn(1)-S(8)#4	81.60(17)
S(2)#13-Ba(3A)-S(2)#22	72.05(11)	S(6)#9-Mn(1)-S(8)#4	81.60(17)
S(2)#10-Ba(3A)-S(2)#22	132.29(3)	S(2)#8-Mn(1)-S(1)#10	89.25(12)
S(2)#21-Ba(3A)-S(2)	132.30(3)	S(2)-Mn(1)-S(1)#10	89.25(12)
S(2)#13-Ba(3A)-S(2)	88.92(8)	S(6)#4-Mn(1)-S(1)#10	88.14(12)
S(2)#10-Ba(3A)-S(2)	88.92(8)	S(6)#9-Mn(1)-S(1)#10	88.14(12)
S(2)#22-Ba(3A)-S(2)	132.29(3)	S(8)#4-Mn(1)-S(1)#10	165.5(2)
S(2)#21-Ba(3A)-S(2)#5	88.92(8)	S(7)#5-Mn(2)-S(7)	96.50(19)
S(2)#13-Ba(3A)-S(2)#5	132.29(3)	S(7)#5-Mn(2)-S(9)	103.86(14)
S(2)#10-Ba(3A)-S(2)#5	132.29(3)	S(7)-Mn(2)-S(9)	103.86(14)
S(2)#22-Ba(3A)-S(2)#5	88.92(8)	S(7)#5-Mn(2)-S(5)#2	92.66(13)
S(2)-Ba(3A)-S(2)#5	72.05(11)	S(7)-Mn(2)-S(5)#2	92.66(13)
S(2)-Ga(1)-S(4)	118.06(14)	S(9)-Mn(2)-S(5)#2	154.9(2)
S(2)-Ga(1)-S(3)	116.38(13)	S(7)#5-Mn(2)-S(6)#5	88.07(16)
S(4)-Ga(1)-S(3)	99.4(2)	S(7)-Mn(2)-S(6)#5	170.86(16)
S(2)-Ga(1)-S(1)	113.59(13)	S(9)-Mn(2)-S(6)#5	82.60(14)
S(4)-Ga(1)-S(1)	100.7(2)	S(5)#2-Mn(2)-S(6)#5	79.19(13)
S(3)-Ga(1)-S(1)	106.61(16)	S(7)#5-Mn(2)-S(6)	170.86(16)
S(7)-Ga(2)-S(4)	110.12(14)	S(7)-Mn(2)-S(6)	88.07(16)
S(7)-Ga(2)-S(8)#4	112.40(15)	S(9)-Mn(2)-S(6)	82.60(14)
S(4)-Ga(2)-S(8)#4	107.1(2)	S(5)#2-Mn(2)-S(6)	79.19(13)
S(7)-Ga(2)-S(5)	110.56(16)	S(6)#5-Mn(2)-S(6)	86.4(3)
S(4)-Ga(2)-S(5)	109.0(2)	S(7)-Mn(3)-S(7)#8	95.81(19)
S(8)#4-Ga(2)-S(5)	107.48(15)	S(7)-Mn(3)-S(8)	95.58(14)
S(11)-Ga(3)-S(6)	123.32(15)	S(7)#8-Mn(3)-S(8)	95.58(14)
S(11)-Ga(3)-S(10)	111.09(15)	S(7)-Mn(3)-S(6)#8	173.81(17)
S(6)-Ga(3)-S(10)	101.4(2)	S(7)#8-Mn(3)-S(6)#8	88.62(16)
S(11)-Ga(3)-S(9)	112.93(15)	S(8)-Mn(3)-S(6)#8	79.64(14)
S(6)-Ga(3)-S(9)	100.1(2)	S(7)-Mn(3)-S(6)	88.62(16)
S(10)-Ga(3)-S(9)	106.15(15)	S(7)#8-Mn(3)-S(6)	173.81(17)

S(8)-Mn(3)-S(6)	79.64(14)	S(11)#8-Mn(5)-S(4)#20	85.90(15)
S(6)#8-Mn(3)-S(6)	86.7(3)	S(11)-Mn(5)-S(4)#17	85.90(14)
S(7)-Mn(3)-S(10)	101.99(15)	S(11)#8-Mn(5)-S(4)#17	176.6(2)
S(7)#8-Mn(3)-S(10)	101.99(15)	S(4)#20-Mn(5)-S(4)#17	92.4(3)
S(8)-Mn(3)-S(10)	153.6(2)	S(11)-Mn(5)-S(10)#17	90.32(14)
S(6)#8-Mn(3)-S(10)	81.24(14)	S(11)#8-Mn(5)-S(10)#17	90.32(14)
S(6)-Mn(3)-S(10)	81.24(14)	S(4)#20-Mn(5)-S(10)#17	86.59(13)
S(2)#22-Mn(4)-S(2)#13	95.02(17)	S(4)#17-Mn(5)-S(10)#17	86.59(13)
S(2)#22-Mn(4)-S(3)	93.76(14)	S(11)-Mn(5)-S(1)#17	100.11(16)
S(2)#13-Mn(4)-S(3)	93.76(14)	S(11)#8-Mn(5)-S(1)#17	100.11(16)
S(2)#22-Mn(4)-S(6)#16	175.93(19)	S(11)#16-Mn(6)-S(4)	85.63(14)
S(2)#13-Mn(4)-S(6)#16	87.52(14)	S(11)#15-Mn(6)-S(4)	175.93(18)
S(3)-Mn(4)-S(6)#16	89.24(12)	S(11)#16-Mn(6)-S(4)#5	175.93(18)
S(2)#22-Mn(4)-S(6)#15	87.52(14)	S(11)#15-Mn(6)-S(4)#5	85.63(14)
S(2)#13-Mn(4)-S(6)#15	175.93(19)	S(4)-Mn(6)-S(4)#5	91.2(3)
S(3)-Mn(4)-S(6)#15	89.24(12)	S(11)#16-Mn(6)-S(9)	94.75(14)
S(6)#16-Mn(4)-S(6)#15	89.8(3)	S(11)#15-Mn(6)-S(9)	94.75(14)
S(2)#22-Mn(4)-S(5)#13	98.22(17)	S(4)-Mn(6)-S(9)	87.62(13)
S(2)#13-Mn(4)-S(5)#13	98.22(17)	S(4)#5-Mn(6)-S(9)	87.62(13)
S(3)-Mn(4)-S(5)#13	162.2(2)	S(11)#16-Mn(6)-S(3)	96.69(16)
S(6)#16-Mn(4)-S(5)#13	78.24(16)	S(11)#15-Mn(6)-S(3)	96.69(16)
S(6)#15-Mn(4)-S(5)#13	78.24(16)	S(4)-Mn(6)-S(3)	80.26(15)
S(11)-Mn(5)-S(11)#8	95.60(18)	S(4)#5-Mn(6)-S(3)	80.26(15)
S(11)-Mn(5)-S(4)#20	176.6(2)	S(9)-Mn(6)-S(3)	162.6(2)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,x-y,-z+2 #2 -y+1,x-y,z #3 -x+y+1,-x+1,-z+2

#4 x,y,-z+2 #5 -x+y+1,-x+1,z #6 -y,x-y,z

#7 -x+y,-x,-z+2 #8 -x+y,-x,z #9 -y,x-y,-z+2

#10 -x+y,-x+1,z #11 -y+1,x-y+1,-z+2 #12 -x+y,-x+1,-z+2

#13 -y+1,x-y+1,z #14 x,y,-z+1 #15 -y+1,x-y,-z+1

#16 -x+y,-x+1,-z+1

Table S4d. Selected distances (Å) and angles (degrees) for PbMn6Ga6S16.

Pb(1)-S(7)#1	3.042(5)	Ga(1)-S(4)	2.280(3)
Pb(1)-S(7)#2	3.042(5)	Ga(1)-S(3)	2.299(5)
Pb(1)-S(7)#3	3.042(5)	Ga(1)-S(2)	2.301(5)
Pb(1)-S(7)	3.042(5)	Ga(2)-S(7)	2.221(4)
Pb(1)-S(7)#4	3.042(5)	Ga(2)-S(4)	2.297(3)
Pb(1)-S(7)#5	3.042(5)	Ga(2)-S(5)	2.312(5)
Pb(1A)-S(7)#6	3.032(5)	Ga(2)-S(6)	2.319(5)
Pb(1A)-S(7)#3	3.032(5)	Ga(3)-S(11)	2.227(4)
Pb(1A)-S(7)#7	3.032(5)	Ga(3)-S(8)	2.268(3)
Pb(1A)-S(7)	3.032(5)	Ga(3)-S(10)	2.320(5)
Pb(1A)-S(7)#8	3.032(5)	Ga(3)-S(9)	2.323(5)
Pb(1A)-S(7)#5	3.032(5)	Mn(1)-S(1)	2.528(6)
Pb(2)-S(1)#1	3.026(5)	Mn(1)-S(1)#1	2.528(6)
Pb(2)-S(1)	3.026(5)	Mn(1)-S(2)#9	2.639(9)
Pb(2)-S(1)#9	3.026(5)	Mn(1)-S(10)#22	2.653(9)
Pb(2)-S(1)#10	3.026(5)	Mn(1)-S(8)#13	2.719(5)
Pb(2)-S(1)#11	3.026(5)	Mn(1)-S(8)#22	2.719(5)
Pb(2)-S(1)#12	3.026(5)	Mn(2)-S(1)	2.524(6)
Pb(2A)-S(1)#6	3.023(5)	Mn(2)-S(1)#6	2.524(6)
Pb(2A)-S(1)	3.023(5)	Mn(2)-S(3)#9	2.644(8)
Pb(2A)-S(1)#13	3.023(5)	Mn(2)-S(9)#9	2.656(9)
Pb(2A)-S(1)#12	3.023(5)	Mn(2)-S(8)#9	2.689(5)
Pb(2A)-S(1)#9	3.023(5)	Mn(2)-S(8)#13	2.689(5)
Pb(2A)-S(1)#14	3.023(5)	Mn(3)-S(7)	2.541(6)
Pb(3)-S(11)#15	3.021(4)	Mn(3)-S(7)#6	2.541(6)
Pb(3)-S(11)#16	3.021(4)	Mn(3)-S(8)#6	2.607(4)
Pb(3)-S(11)#17	3.021(4)	Mn(3)-S(8)	2.607(4)
Pb(3)-S(11)#18	3.021(4)	Mn(3)-S(5)#3	2.633(8)
Pb(3)-S(11)#19	3.021(4)	Mn(3)-S(3)	2.694(9)
Pb(3)-S(11)	3.021(4)	Mn(4)-S(7)	2.545(6)
Pb(3A)-S(11)#20	3.028(4)	Mn(4)-S(7)#1	2.546(6)
Pb(3A)-S(11)#18	3.028(4)	Mn(4)-S(6)#3	2.614(8)
Pb(3A)-S(11)#15	3.028(4)	Mn(4)-S(8)#6	2.648(4)
Pb(3A)-S(11)#21	3.028(4)	Mn(4)-S(8)#23	2.648(4)
Pb(3A)-S(11)#6	3.028(4)	Mn(4)-S(2)	2.699(9)
Pb(3A)-S(11)	3.028(4)	Mn(5)-S(11)#6	2.522(5)
Ga(1)-S(1)	2.243(4)	Mn(5)-S(11)	2.522(5)

Mn(5)-S(4)#3	2.604(4)	S(7)-Pb(1A)-S(7)#5	86.69(15)
Mn(5)-S(4)#7	2.604(4)	S(7)#8-Pb(1A)-S(7)#5	75.1(2)
Mn(5)-S(9)#15	2.639(8)	S(1)#1-Pb(2)-S(1)	75.8(2)
Mn(5)-S(5)#3	2.782(9)	S(1)#1-Pb(2)-S(1)#9	133.54(7)
Mn(6)-S(11)	2.512(5)	S(1)-Pb(2)-S(1)#9	86.19(15)
Mn(6)-S(11)#19	2.512(5)	S(1)#1-Pb(2)-S(1)#10	86.19(15)
Mn(6)-S(4)#7	2.570(4)	S(1)-Pb(2)-S(1)#10	133.54(7)
Mn(6)-S(4)#24	2.570(4)	S(1)#9-Pb(2)-S(1)#10	133.54(7)
Mn(6)-S(10)#15	2.623(9)	S(1)#1-Pb(2)-S(1)#11	86.19(15)
Mn(6)-S(6)#24	2.785(9)	S(1)-Pb(2)-S(1)#11	133.54(7)
S(7)#1-Pb(1)-S(7)#2	86.33(14)	S(1)#9-Pb(2)-S(1)#11	75.8(2)
S(7)#1-Pb(1)-S(7)#3	133.47(7)	S(1)#10-Pb(2)-S(1)#11	86.19(15)
S(7)#2-Pb(1)-S(7)#3	75.6(2)	S(1)#1-Pb(2)-S(1)#12	133.54(7)
S(7)#1-Pb(1)-S(7)	75.6(2)	S(1)-Pb(2)-S(1)#12	86.19(15)
S(7)#2-Pb(1)-S(7)	133.47(7)	S(1)#9-Pb(2)-S(1)#12	86.19(15)
S(7)#3-Pb(1)-S(7)	86.33(14)	S(1)#10-Pb(2)-S(1)#12	75.8(2)
S(7)#1-Pb(1)-S(7)#4	86.33(14)	S(1)#11-Pb(2)-S(1)#12	133.54(7)
S(7)#2-Pb(1)-S(7)#4	86.33(14)	S(1)#6-Pb(2A)-S(1)	75.7(2)
S(7)#3-Pb(1)-S(7)#4	133.47(7)	S(1)#6-Pb(2A)-S(1)#13	86.30(15)
S(7)-Pb(1)-S(7)#4	133.47(7)	S(1)-Pb(2A)-S(1)#13	133.49(7)
S(7)#1-Pb(1)-S(7)#5	133.47(7)	S(1)#6-Pb(2A)-S(1)#12	133.49(7)
S(7)#2-Pb(1)-S(7)#5	133.47(7)	S(1)-Pb(2A)-S(1)#12	86.30(15)
S(7)#3-Pb(1)-S(7)#5	86.33(14)	S(1)#13-Pb(2A)-S(1)#12	133.48(7)
S(7)-Pb(1)-S(7)#5	86.33(14)	S(1)#6-Pb(2A)-S(1)#9	133.49(7)
S(7)#4-Pb(1)-S(7)#5	75.6(2)	S(1)-Pb(2A)-S(1)#9	86.30(15)
S(7)#6-Pb(1A)-S(7)#3	133.31(7)	S(1)#13-Pb(2A)-S(1)#9	75.7(2)
S(7)#6-Pb(1A)-S(7)#7	86.69(15)	S(1)#12-Pb(2A)-S(1)#9	86.30(15)
S(7)#3-Pb(1A)-S(7)#7	75.1(2)	S(1)#6-Pb(2A)-S(1)#14	86.30(15)
S(7)#6-Pb(1A)-S(7)	75.1(2)	S(1)-Pb(2A)-S(1)#14	133.49(7)
S(7)#3-Pb(1A)-S(7)	86.69(15)	S(1)#13-Pb(2A)-S(1)#14	86.30(15)
S(7)#7-Pb(1A)-S(7)	133.31(7)	S(1)#12-Pb(2A)-S(1)#14	75.7(2)
S(7)#6-Pb(1A)-S(7)#8	86.69(15)	S(1)#9-Pb(2A)-S(1)#14	133.48(7)
S(7)#3-Pb(1A)-S(7)#8	133.31(7)	S(11)#15-Pb(3)-S(11)#16	133.46(6)
S(7)#7-Pb(1A)-S(7)#8	86.69(15)	S(11)#15-Pb(3)-S(11)#17	75.61(19)
S(7)-Pb(1A)-S(7)#8	133.31(7)	S(11)#16-Pb(3)-S(11)#17	86.36(14)
S(7)#6-Pb(1A)-S(7)#5	133.31(7)	S(11)#15-Pb(3)-S(11)#18	86.36(14)
S(7)#3-Pb(1A)-S(7)#5	86.69(15)	S(11)#16-Pb(3)-S(11)#18	75.61(19)
S(7)#7-Pb(1A)-S(7)#5	133.31(7)	S(11)#17-Pb(3)-S(11)#18	133.46(6)

S(11)#15-Pb(3)-S(11)#19	133.46(6)	S(8)-Ga(3)-S(10)	100.1(2)
S(11)#16-Pb(3)-S(11)#19	86.36(14)	S(11)-Ga(3)-S(9)	112.0(2)
S(11)#17-Pb(3)-S(11)#19	86.36(14)	S(8)-Ga(3)-S(9)	99.5(2)
S(11)#18-Pb(3)-S(11)#19	133.46(6)	S(10)-Ga(3)-S(9)	106.23(14)
S(11)#15-Pb(3)-S(11)	86.36(14)	S(1)-Mn(1)-S(1)#1	94.7(3)
S(11)#16-Pb(3)-S(11)	133.46(6)	S(1)-Mn(1)-S(2)#9	94.34(19)
S(11)#17-Pb(3)-S(11)	133.46(6)	S(1)#1-Mn(1)-S(2)#9	94.34(19)
S(11)#18-Pb(3)-S(11)	86.36(14)	S(1)-Mn(1)-S(10)#22	103.33(18)
S(11)#19-Pb(3)-S(11)	75.61(19)	S(1)#1-Mn(1)-S(10)#22	103.33(18)
S(11)#20-Pb(3A)-S(11)#18	133.56(6)	S(2)#9-Mn(1)-S(10)#22	153.7(3)
S(11)#20-Pb(3A)-S(11)#15	75.91(19)	S(1)-Mn(1)-S(8)#13	88.57(13)
S(11)#18-Pb(3A)-S(11)#15	86.14(14)	S(1)#1-Mn(1)-S(8)#13	173.0(2)
S(11)#20-Pb(3A)-S(11)#21	86.14(14)	S(2)#9-Mn(1)-S(8)#13	79.29(16)
S(11)#18-Pb(3A)-S(11)#21	75.91(19)	S(10)#22-Mn(1)-S(8)#13	81.79(18)
S(11)#15-Pb(3A)-S(11)#21	133.56(6)	S(1)-Mn(1)-S(8)#22	173.0(2)
S(11)#20-Pb(3A)-S(11)#6	86.14(14)	S(1)#1-Mn(1)-S(8)#22	88.58(13)
S(11)#18-Pb(3A)-S(11)#6	133.56(6)	S(2)#9-Mn(1)-S(8)#22	79.29(16)
S(11)#15-Pb(3A)-S(11)#6	133.56(6)	S(10)#22-Mn(1)-S(8)#22	81.79(18)
S(11)#21-Pb(3A)-S(11)#6	86.14(14)	S(8)#13-Mn(1)-S(8)#22	87.50(19)
S(11)#20-Pb(3A)-S(11)	133.56(6)	S(1)-Mn(2)-S(1)#6	94.6(3)
S(11)#18-Pb(3A)-S(11)	86.14(14)	S(1)-Mn(2)-S(3)#9	93.63(19)
S(11)#15-Pb(3A)-S(11)	86.14(14)	S(1)#6-Mn(2)-S(3)#9	93.63(19)
S(11)#21-Pb(3A)-S(11)	133.56(6)	S(1)-Mn(2)-S(9)#9	103.74(18)
S(11)#6-Pb(3A)-S(11)	75.91(19)	S(1)#6-Mn(2)-S(9)#9	103.74(18)
S(1)-Ga(1)-S(4)	112.36(13)	S(3)#9-Mn(2)-S(9)#9	154.2(3)
S(1)-Ga(1)-S(3)	111.1(3)	S(1)-Mn(2)-S(8)#9	172.1(2)
S(4)-Ga(1)-S(3)	107.5(2)	S(1)#6-Mn(2)-S(8)#9	89.33(14)
S(1)-Ga(1)-S(2)	111.8(3)	S(3)#9-Mn(2)-S(8)#9	79.22(16)
S(4)-Ga(1)-S(2)	106.0(2)	S(9)#9-Mn(2)-S(8)#9	81.95(17)
S(3)-Ga(1)-S(2)	107.70(14)	S(1)-Mn(2)-S(8)#13	89.33(14)
S(7)-Ga(2)-S(4)	120.19(13)	S(1)#6-Mn(2)-S(8)#13	172.1(2)
S(7)-Ga(2)-S(5)	114.3(3)	S(3)#9-Mn(2)-S(8)#13	79.22(16)
S(4)-Ga(2)-S(5)	99.6(2)	S(9)#9-Mn(2)-S(8)#13	81.95(17)
S(7)-Ga(2)-S(6)	115.6(2)	S(8)#9-Mn(2)-S(8)#13	85.98(19)
S(4)-Ga(2)-S(6)	98.1(2)	S(7)-Mn(3)-S(7)#6	93.4(3)
S(5)-Ga(2)-S(6)	106.66(15)	S(7)-Mn(3)-S(8)#6	88.61(13)
S(11)-Ga(3)-S(8)	124.62(13)	S(7)#6-Mn(3)-S(8)#6	177.78(19)
S(11)-Ga(3)-S(10)	112.2(2)	S(7)-Mn(3)-S(8)	177.78(19)

S(7)#6-Mn(3)-S(8)	88.61(13)	S(11)-Mn(5)-S(4)#3	177.8(2)
S(8)#6-Mn(3)-S(8)	89.40(19)	S(11)#6-Mn(5)-S(4)#7	177.8(2)
S(7)-Mn(3)-S(5)#3	90.95(19)	S(11)-Mn(5)-S(4)#7	86.10(13)
S(7)#6-Mn(3)-S(5)#3	90.95(19)	S(4)#3-Mn(5)-S(4)#7	92.56(19)
S(8)#6-Mn(3)-S(5)#3	88.0(2)	S(11)#6-Mn(5)-S(9)#15	92.15(17)
S(8)-Mn(3)-S(5)#3	88.0(2)	S(11)-Mn(5)-S(9)#15	92.15(17)
S(7)-Mn(3)-S(3)	100.83(17)	S(4)#3-Mn(5)-S(9)#15	85.96(16)
S(7)#6-Mn(3)-S(3)	100.83(17)	S(4)#7-Mn(5)-S(9)#15	85.96(16)
S(8)#6-Mn(3)-S(3)	79.78(18)	S(11)#6-Mn(5)-S(5)#3	100.02(17)
S(8)-Mn(3)-S(3)	79.77(18)	S(11)-Mn(5)-S(5)#3	100.02(17)
S(5)#3-Mn(3)-S(3)	162.7(3)	S(4)#3-Mn(5)-S(5)#3	81.54(16)
S(7)-Mn(4)-S(7)#1	94.2(3)	S(4)#7-Mn(5)-S(5)#3	81.54(16)
S(7)-Mn(4)-S(6)#3	92.16(19)	S(9)#15-Mn(5)-S(5)#3	161.9(3)
S(7)#1-Mn(4)-S(6)#3	92.16(19)	S(11)-Mn(6)-S(11)#19	95.0(2)
S(7)-Mn(4)-S(8)#6	87.63(13)	S(11)-Mn(6)-S(4)#7	87.02(13)
S(7)#1-Mn(4)-S(8)#6	178.13(18)	S(11)#19-Mn(6)-S(4)#7	177.90(19)
S(6)#3-Mn(4)-S(8)#6	87.85(19)	S(11)-Mn(6)-S(4)#24	177.90(19)
S(7)-Mn(4)-S(8)#23	178.13(18)	S(11)#19-Mn(6)-S(4)#24	87.02(13)
S(7)#1-Mn(4)-S(8)#23	87.63(13)	S(4)#7-Mn(6)-S(4)#24	90.94(19)
S(6)#3-Mn(4)-S(8)#23	87.85(19)	S(11)-Mn(6)-S(10)#15	93.09(17)
S(8)#6-Mn(4)-S(8)#23	90.50(19)	S(11)#19-Mn(6)-S(10)#15	93.09(17)
S(7)-Mn(4)-S(2)	100.07(17)	S(4)#7-Mn(6)-S(10)#15	86.28(17)
S(7)#1-Mn(4)-S(2)	100.07(17)	S(4)#24-Mn(6)-S(10)#15	86.28(17)
S(6)#3-Mn(4)-S(2)	161.9(3)	S(11)-Mn(6)-S(6)#24	99.07(17)
S(8)#6-Mn(4)-S(2)	79.49(18)	S(11)#19-Mn(6)-S(6)#24	99.07(17)
S(8)#23-Mn(4)-S(2)	79.49(18)	S(4)#7-Mn(6)-S(6)#24	81.10(16)
S(11)#6-Mn(5)-S(11)	95.2(2)	S(4)#24-Mn(6)-S(6)#24	81.10(16)
S(11)#6-Mn(5)-S(4)#3	86.10(13)	S(10)#15-Mn(6)-S(6)#24	161.9(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,-z+2 #2 -y+1,x-y+1,-z+2 #3 -y+1,x-y+1,z
#4 -x+y,-x+1,-z+2 #5 -x+y,-x+1,z #6 x,y,-z+1
#7 -y+1,x-y+1,-z+1 #8 -x+y,-x+1,-z+1 #9 -y,x-y,z
#10 -x+y,-x,-z+2 #11 -y,x-y,-z+2 #12 -x+y,-x,z
#13 -y,x-y,-z+1 #14 -x+y,-x,-z+1 #15 -x+y+1,-x+1,z
#16 -y+1,x-y,-z #17 -x+y+1,-x+1,-z #18 -y+1,x-y,z
#19 x,y,-z #20 -x+y+1,-x+1,-z+1 #21 -y+1,x-y,-z+1
#22 -y,x-y,z+1 #23 x,y,z+1 #24 -y+1,x-y+1,z-1
#25 -x+y,-x+1,z+1 #26 x,y,z-1 #27 -x+y,-x,z-1

Table S5a. Bond length (l (Å)), the average bond length (L (Å)) and distortion degree (Δd) of MnS_6 or MgS_6 octahedra in $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb), La_3MnGaS_7, $La_6MnGe_2S_{14}$ and $AeMg_6Ga_6S_{16}$ (Ae=Ca, Sr, Ba).

Compounds	Octahedral	Bond	l/Å						L/Å	Δd%
$CaMn_6Ga_6S_{16}$	$Mn(1)S_6$	Mn-S	2.534	2.534	2.604	2.669	2.73	2.73	2.6335	0.676%
	$Mn(2)S_6$	Mn-S	2.53	2.53	2.626	2.675	2.703	2.703	2.6278	0.545%
	$Mn(3)S_6$	Mn-S	2.556	2.556	2.612	2.612	2.655	2.67	2.6101	0.191%
	$Mn(4)S_6$	Mn-S	2.556	2.556	2.598	2.659	2.659	2.709	2.6228	0.327%
	$Mn(5)S_6$	Mn-S	2.523	2.523	2.576	2.624	2.624	2.797	2.6111	0.861%
	$Mn(6)S_6$	Mn-S	2.516	2.516	2.588	2.588	2.657	2.73	2.5991	0.578%
$SrMn_6Ga_6S_{16}$	$Mn(1)S_6$	Mn-S	2.518	2.518	2.582	2.582	2.703	2.755	2.6096	0.803%
	$Mn(2)S_6$	Mn-S	2.501	2.501	2.598	2.611	2.611	2.818	2.6066	1.120%
	$Mn(3)S_6$	Mn-S	2.544	2.544	2.611	2.611	2.679	2.699	2.6146	0.354%
	$Mn(4)S_6$	Mn-S	2.522	2.522	2.651	2.697	2.707	2.707	2.6343	0.667%
	$Mn(5)S_6$	Mn-S	2.531	2.531	2.602	2.653	2.653	2.728	2.6163	0.499%
	$Mn(6)S_6$	Mn-S	2.514	2.514	2.628	2.68	2.723	2.723	2.6303	0.779%
$BaMn_6Ga_6S_{16}$	$Mn(1)S_6$	Mn-S	2.527	2.527	2.632	2.632	2.653	2.719	2.6150	0.472%
	$Mn(2)S_6$	Mn-S	2.505	2.505	2.607	2.707	2.723	2.723	2.6283	0.917%
	$Mn(3)S_6$	Mn-S	2.495	2.495	2.685	2.707	2.707	2.744	2.6388	1.064%
	$Mn(4)S_6$	Mn-S	2.506	2.506	2.617	2.64	2.64	2.84	2.6248	1.251%
	$Mn(5)S_6$	Mn-S	2.505	2.505	2.573	2.573	2.744	2.808	2.6180	1.359%
	$Mn(6)S_6$	Mn-S	2.481	2.481	2.608	2.608	2.649	2.849	2.6126	1.531%
$PbMn_6Ga_6S_{16}$	$Mn(1)S_6$	Mn-S	2.528	2.528	2.639	2.653	2.719	2.719	2.6310	0.621%
	$Mn(2)S_6$	Mn-S	2.524	2.524	2.644	2.656	2.689	2.689	2.6210	0.497%
	$Mn(3)S_6$	Mn-S	2.541	2.541	2.607	2.607	2.633	2.694	2.6038	0.282%
	$Mn(4)S_6$	Mn-S	2.545	2.546	2.614	2.648	2.648	2.699	2.6166	0.315%
	$Mn(5)S_6$	Mn-S	2.522	2.522	2.604	2.604	2.639	2.782	2.6121	0.659%
	$Mn(6)S_6$	Mn-S	2.512	2.512	2.57	2.57	2.623	2.785	2.5953	0.865%
La_3MnGaS_7	MnS_6	Mn-S	2.6218	2.6218	2.6218	2.5806	2.5806	2.5806	2.6012	0.042%
$La_6MnGe_2S_{14}$	MnS_6	Mn-S	2.6417	2.6417	2.6417	2.6794	2.6794	2.6794	2.6606	0.036%
$CaMg_6Ga_6S_{16}$	Mg(1)S6	Mg-S	2.513	2.513	2.558	2.558	2.646	2.729	2.586	0.605%
	$Mg(2)S_6$	Mg-S	2.508	2.508	2.527	2.605	2.605	2.78	2.589	0.899%
	$Mg(3)S_6$	Mg-S	2.534	2.534	2.604	2.604	2.631	2.667	2.596	0.235%
	$Mg(4)S_6$	Mg-S	2.544	2.544	2.582	2.655	2.655	2.701	2.614	0.363%
	$Mg(5)S_6$	Mg-S	2.518	2.518	2.615	2.664	2.681	2.681	2.613	0.498%
	$Mg_{(6)}S_6$	Mg-S	2.525	2.525	2.596	2.669	2.712	2.712	2.623	0.632%
	$Mg(1)S_6$	Mg-S	2.506	2.506	2.56	2.56	2.678	2.758	2.595	0.863%
	$Mg(2)S_6$	Mg-S	2.499	2.499	2.589	2.589	2.606	2.779	2.594	0.874%

$SrMg_6Ga_6S_{16}$	$Mg(3)S_6$	Mg-S	2.52	2.52	2.606	2.606	2.661	2.705	2.603	0.459%
	$Mg(4)S_6$	Mg-S	2.524	2.524	2.642	2.642	2.593	2.705	2.605	0.433%
	$Mg(5)S_6$	Mg-S	2.525	2.525	2.678	2.678	2.617	2.714	2.623	0.560%
	$Mg_{(6)}S_6$	Mg-S	2.496	2.496	2.717	2.717	2.699	2.61	2.623	0.931%
$BaMg_6Ga_6S_{16}$	$Mg(1)S_6$	Mg-S	2.504	2.504	2.552	2.552	2.737	2.757	2.601	1.101%
	$Mg(2)S_6$	Mg-S	2.467	2.467	2.592	2.592	2.63	2.821	2.595	1.418%
	$Mg(3)S_6$	Mg-S	2.507	2.507	2.614	2.614	2.711	2.721	2.612	0.729%
	$Mg(4)S_6$	Mg-S	2.498	2.498	2.632	2.632	2.634	2.72	2.602	0.640%
	$Mg(5)S_6$	Mg-S	2.5	2.5	2.643	2.686	2.686	2.775	2.632	1.020%
	$Mg_{(6)}S_6$	Mg-S	2.481	2.481	2.637	2.675	2.691	2.691	2.609	0.856%

Table S5b. Bond length (l (Å)), the average bond length (L (Å)) and distortion degree (Δd) of GaS_4 tetrahedra in $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb), La_3MnGaS_7, $LiGaS_2$, α-$BaGa_4S_7$ and $AeMg_6Ga_6S_{16}$ (Ae=Ca, Sr, Ba).

Compounds	Tetrahedron	Bond	l/Å				L/Å	Δd%
$CaMn_6Ga_6S_{16}$	$Ga(1)S_4$	Ga-S	2.212	2.229	2.312	2.320	2.2682	0.232%
	$Ga(2)S_4$	Ga-S	2.227	2.275	2.324	2.336	2.2905	0.187%
	$Ga(3)S_4$	Ga-S	2.226	2.275	2.297	2.297	2.2737	0.084%
$SrMn_6Ga_6S_{16}$	$Ga(1)S_4$	Ga-S	2.224	2.269	2.321	2.338	2.2880	0.201%
	$Ga(2)S_4$	Ga-S	2.235	2.284	2.298	2.306	2.2807	0.076%
	$Ga(3)S_4$	Ga-S	2.219	2.299	2.308	2.327	2.2882	0.170%
$BaMn_6Ga_6S_{16}$	$Ga(1)S_4$	Ga-S	2.223	2.298	2.32	2.322	2.2907	0.162%
	$Ga(2)S_4$	Ga-S	2.234	2.287	2.301	2.314	2.2840	0.093%
	$Ga(3)S_4$	Ga-S	2.225	2.26	2.326	2.328	2.2847	0.194%
$PbMn_6Ga_6S_{16}$	$Ga(1)S_4$	Ga-S	2.243	2.28	2.299	2.301	2.2807	0.052%
	$Ga(2)S_4$	Ga-S	2.221	2.297	2.312	2.319	2.2872	0.152%
	$Ga(3)S_4$	Ga-S	2.227	2.268	2.32	2.323	2.2845	0.158%
La_3MnGaS_7	GaS_4	Ga-S	2.226	2.279	2.279	2.279	2.268	0.052%
$CaMg_6Ga_6S_{16}$	Ga(1)S4	Ga-S	2.223	2.273	2.294	2.295	2.271	0.085%
	Ga(2)S4	Ga-S	2.212	2.29	2.308	2.317	2.282	0.172%
	Ga(3)S4	Ga-S	2.217	2.264	2.312	2.329	2.281	0.191%
$SrMg_6Ga_6S_{16}$	Ga(1)S4	Ga-S	2.224	2.277	2.29	2.216	2.252	0.104%
	Ga(2)S4	Ga-S	2.216	2.289	2.313	2.314	2.283	0.160%
	Ga(3)S4	Ga-S	2.216	2.267	2.313	2.34	2.284	0.222%
$BaMg_6Ga_6S_{16}$	Ga(1)S4	Ga-S	2.223	2.281	2.298	2.301	2.276	0.099%
	Ga(2)S4	Ga-S	2.215	2.294	2.297	2.33	2.284	0.179%
	Ga(3)S4	Ga-S	2.212	2.271	2.326	2.336	2.286	0.245%
$LiGaS_2$	GaS4	Ga-S	2.278	2.269	2.28	2.281	2.278	0.002%

α-$BaGa_4S_7$	Ga(1)S4	Ga-S	2.338	2.325	2.229	2.229	2.281	0.268%
	Ga(2)S4	Ga-S	2.256	2.271	2.324	2.247	2.275	0.089%

Table S6. The diameters of three size of channels in compounds

Compounds	Small size	Medium size	Maximum size
$AgMg_3Ga_3S_8$	5.9974	6.1638	6.1966
$LiMg_3Ga_3S_8$	6.4100	6.4286	6.5322
$NaMg_3Ga_3S_8$	6.4873	6.5144	6.6227
$CaMg_6Ga_6S_{16}$	6.5402	6.5556	6.6681
$CaMn_6Ga_6S_{16}$	6.5438	6.5642	6.6841

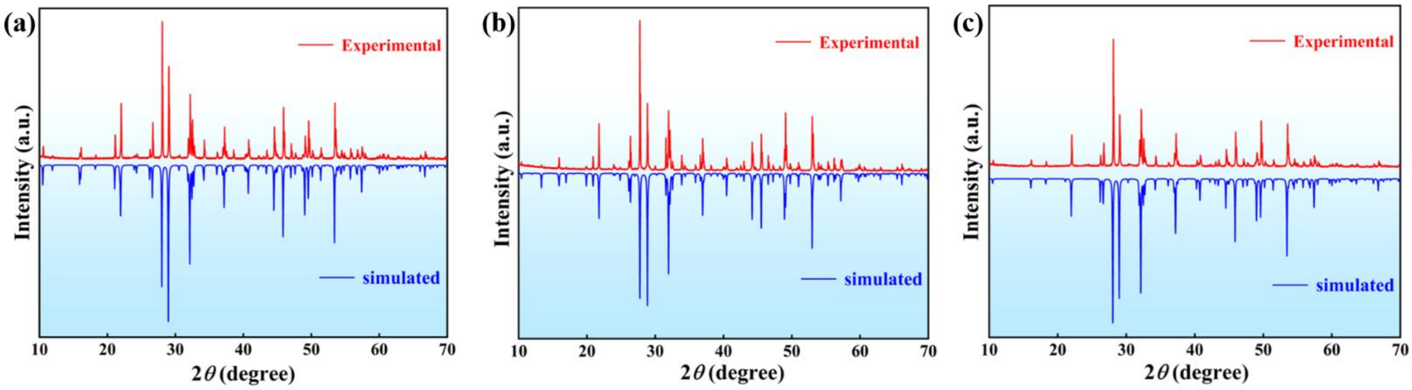

Figure S1. Experimental and simulated powder X-ray diffraction patterns of compounds $SrMn_6Ga_6S_{16}$(a), $BaMn_6Ga_6S_{16}$ (b) and $PbMn_6Ga_6S_{16}$(c).

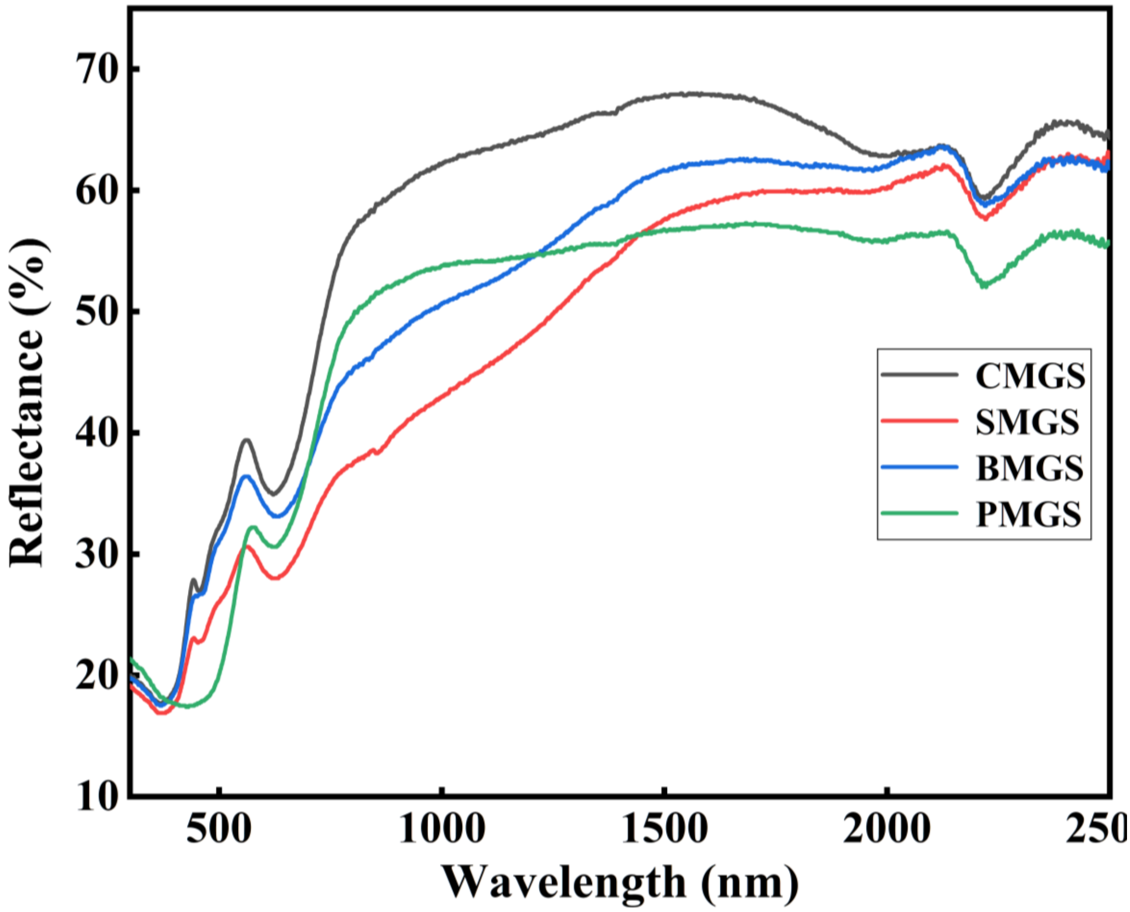

Figure S2. The UV−vis−NIR diffuse reflectance spectra for $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb).

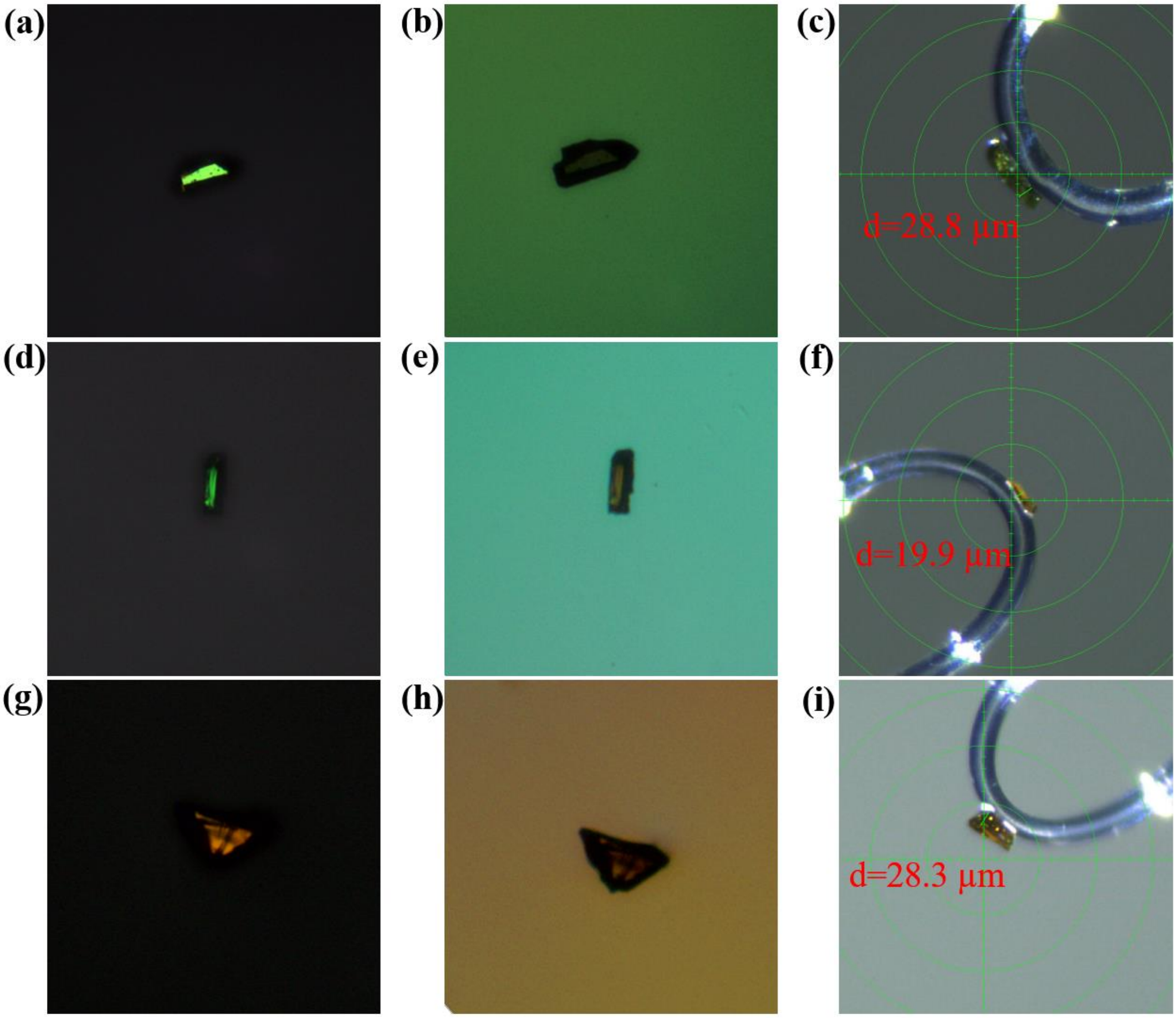

Figure S3. (a-c) The original interference color, extinction, and thickness of the $SrMn_6Ga_6S_{16}$ crystal, respectively; (d-f) The original interference color, extinction, and thickness of the $BaMn_6Ga_6S_{16}$ crystal, respectively; (g-i) The original interference color, extinction, and thickness of the $PbMn_6Ga_6S_{16}$ crystal, respectively.

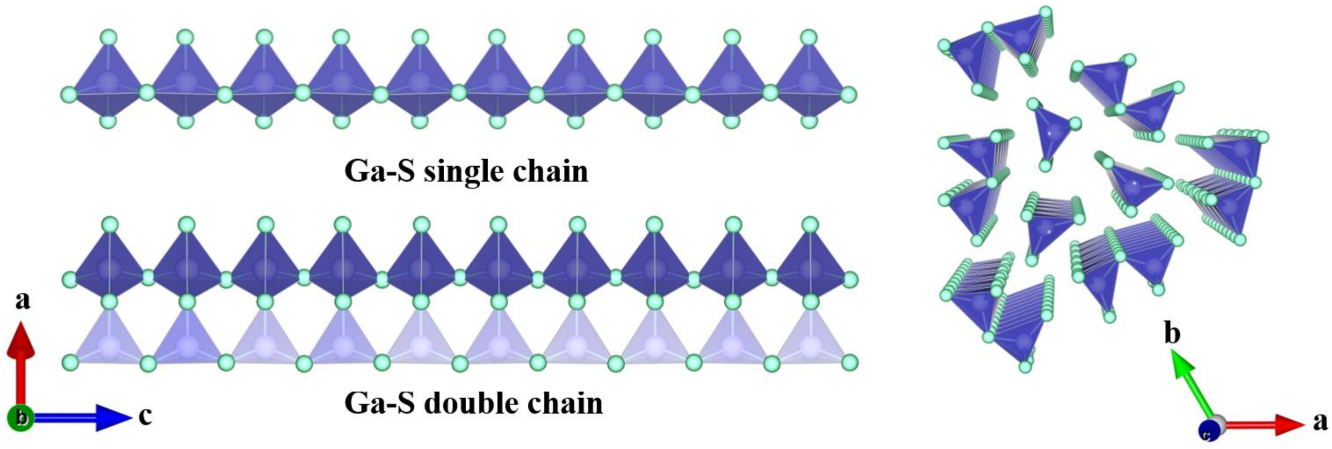

Figure S4. The arrangement of GaS_4 tetrahedra in the structure of $MMn_6Ga_6S_{16}$ (M=Ca, Sr, Ba, Pb).

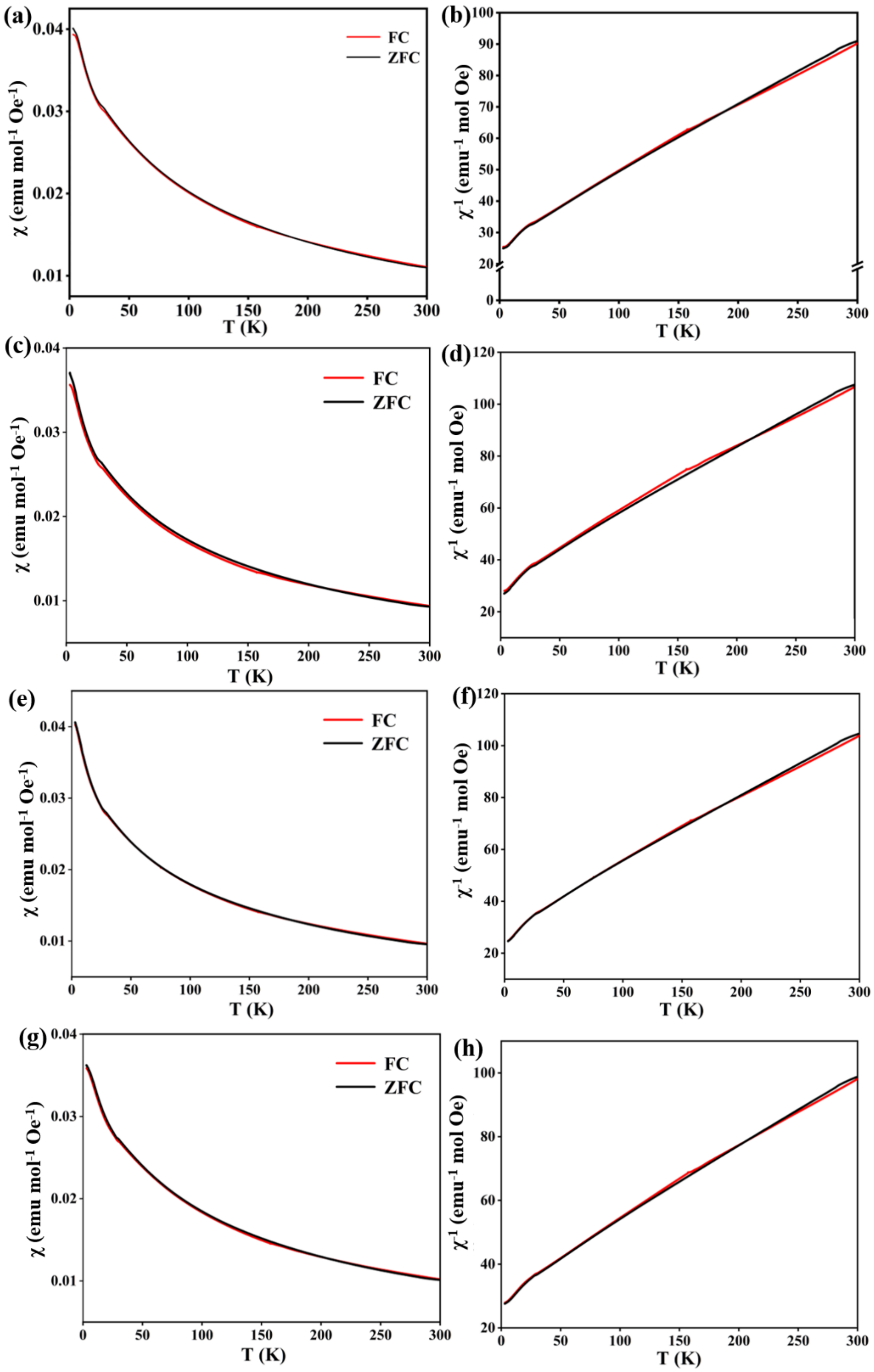

Figure S5. The magnetization curve of $CaMn_6Ga_6S_{16}$ (a), $SrMn_6Ga_6S_{16}$ (c), $BaMn_6Ga_6S_{16}$ (e) and $PbMn_6Ga_6S_{16}$ (g) under zero-field-cooling (ZFC) and field cooling (FC). b d f h) shows the plots of inverse of susceptibility(1/χ) versus temperature (T).

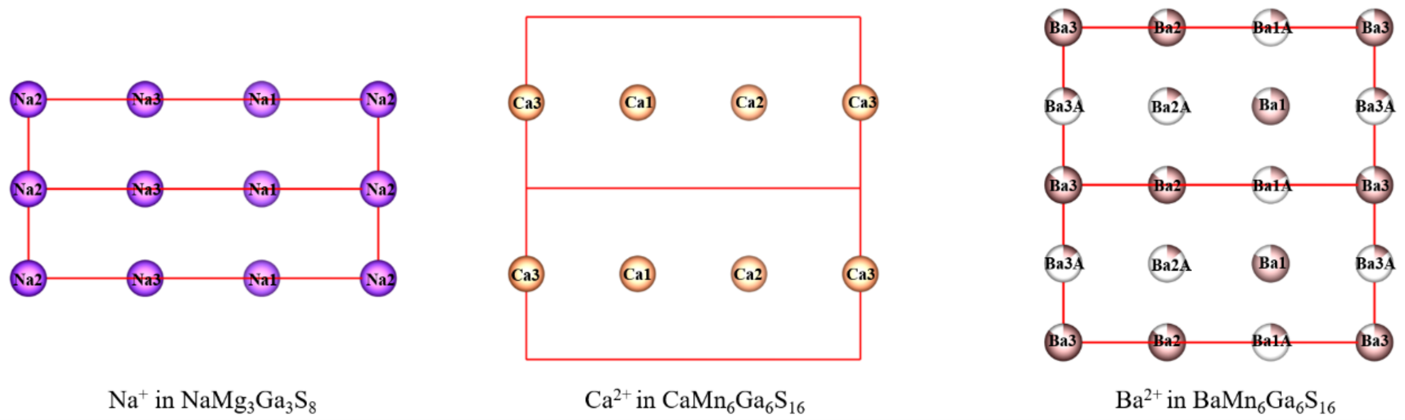

Figure S6. The arrangement of A-site cations in compounds $NaMg_3Ga_3S_8$, $CaMn_6Ga_6S_{16}$ and $BaMn_6Ga_6S_{16}$.