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A novel monoclinic phase of impurity-doped CaGa_2S_4 as a phosphor with high emission intensity

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Key indicators: single-crystal X-ray study; $T = 270$ K; mean $\sigma(\text{Ga}-\text{S}) = 0.001$ Å; R factor = 0.038; wR factor = 0.050; data-to-parameter ratio = 49.1.

In the solid-state synthesis of impurity-doped CaGa_2S_4 , calcium tetrathiodigallate(III), a novel phosphor material (denominated as the X -phase), with monoclinic symmetry in the space group $P2_1/a$, has been discovered. Its emission intensity is higher than that of the known orthorhombic polymorph of CaGa_2S_4 crystallizing in the space group $Fddd$. The asymmetric unit of the monoclinic phase consists of two Ca, four Ga and eight S sites. Each of the Ca and Ga atoms is surrounded by seven and four sulfide ions, respectively, thereby sharing each of the sulfur sites with the nearest neighbours. In contrast, the corresponding sites in the orthorhombic phase are surrounded by eight and four S atoms, respectively. The photoluminescence peaks from Mn^{2+} and Ce^{3+} in the doped X -phase, both of which are supposed to replace Ca^{2+} ions, have been observed to shift towards the high energy side in comparison with those in the orthorhombic phase. This suggests that the crystal field around the Mn^{2+} and Ce^{3+} ions in the X -phase is weaker than that in the orthorhombic phase.

Related literature

For the crystal structure of the orthorhombic form of CaGa_2S_4 , see: Eisenmann *et al.* (1983). For the emission properties of CaGa_2S_4 , see: Peters & Baglio (1972); Georgobiani *et al.* (1995); Bessière *et al.* (2004); Takizawa & Hidaka (2008). For synthetic details, see: Boitier *et al.* (2009); Obonai *et al.* (2009). For the Mn^{2+} emission properties in various compounds, see: Barthou *et al.* (1994); Provenzano & White (1991); Wang *et al.* (2003). For crystallographic background, see: Carruthers & Watkin (1979).

Experimental

Crystal data

CaGa_2S_4	$V = 1262.9$ (8) Å ³
$M_r = 307.76$	$Z = 8$
Monoclinic, $P2_1/a$	Mo $K\alpha$ radiation
$a = 6.841$ (3) Å	$\mu = 10.52$ mm ⁻¹
$b = 27.069$ (9) Å	$T = 270$ K
$c = 7.231$ (3) Å	$0.10 \times 0.10 \times 0.05$ mm
$\beta = 109.413$ (5)°	

Data collection

Rigaku Saturn724+ diffractometer	8869 measured reflections
Absorption correction: multi-scan (<i>REQABS</i> ; Jacobson, 1998)	2869 independent
$T_{\min} = 0.417$, $T_{\max} = 0.591$	256 reflections with $F^2 > 2\sigma(F^2)$
	$R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	127 parameters
$wR(F^2) = 0.050$	$\Delta\rho_{\max} = 2.64$ e Å ⁻³
$S = 1.21$	$\Delta\rho_{\min} = -3.10$ e Å ⁻³
2869 reflections	

Data collection: *CrystalClear* (Rigaku/MSD and Rigaku, 2006); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSD and Rigaku, 2006); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *VESTA 3* (Momma & Izumi, 2011); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSD and Rigaku, 2006).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2605).

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supplementary materials

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A novel monoclinic phase of impurity-doped CaGa_2S_4 as a phosphor with high emission intensity

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Comment

The alkaline earth thiodigallates $M\text{Ga}_2\text{S}_4$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) have been studied as candidates for phosphor host materials because of their various emissions when doped with a rare earth element (Peters & Baglio, 1972; Georgobiani *et al.*, 1995; Bessière *et al.*, 2004; Takizawa & Hidaka, 2008). Especially, CaGa_2S_4 doped with Ce^{3+} and Eu^{2+} shows strong blue and green emissions. This compound normally belongs to the orthorhombic system, crystallizing in space group $Fddd$ (Eisenmann *et al.*, 1983). However, in the synthesis of CaGa_2S_4 using solid state reactions, a novel phosphor (we call it the X -phase) has unexpectedly appeared. In this paper, the crystal structure of the X -phase investigated by powder and single-crystal X-ray diffraction (XRD) measurements is reported.

Powder XRD patterns of the X -phase are shown in Fig. 1. This phase happened to be generated when doped with one of the impurities such as Mn, Ge, Sn, La, Ce, Nd, Sm, Dy, intentionally incorporated as an activator of fluorescence or phosphorescence. Thus it is expected that the X -phase is strongly related with the dopant. However, detailed conditions how to prepare the X -phase from a directed preparation route have not been clarified yet. From the analysis of the single-crystal XRD data, the chemical formula of the compound in the X -phase was shown to be CaGa_2S_4 . The simulation of the powder XRD pattern corresponds well to the experimental pattern as shown in Fig. 1. Hence we can conclude that the X -phase is a newly found polymorph of CaGa_2S_4 .

The unit cell of the X -phase is shown in Figs. 2 and 3; the asymmetric unit consists of two Ca sites, four Ga sites and seven S sites. Figs. 4 and 5 show the environment of the cation sites in the unit cell. In the X -phase, each Ca site is surrounded by seven sulfur atoms forming a distorted enneahedron. Each of the involved sulfur atoms is shared by the adjacent one or two Ca sites and by two Ga sites. The Ca—S distances range from 2.8261 (10) to 3.0823 (13) Å. Each Ga site is tetrahedrally surrounded by sulfur atoms which are also shared by adjacent two Ca sites and two Ga sites. The Ga—S distances and the S—Ga—S angles range from 2.2254 (11) to 2.3116 (11) Å and from 93.54 (3) to 124.12 (3)°, respectively. In the orthorhombic phase, each of the three Ca sites and the two Ga sites is in an eightfold and fourfold coordination environment, respectively, by sulfur atoms. Each of the sulfur atoms of these sites is shared by adjacent two Ca sites and two Ga sites. The Ca—S distances in this polymorph range from 2.970 to 3.130 Å. The Ga—S distances and the S—Ga—S angles range from 2.240 to 2.318 Å and from 96.6 to 125°. It should be noted that the coordination number of the Ca sites in the X -phase is reduced by one compared to that of the orthorhombic phase, while the Ga sites are tetrahedrally surrounded in both phases. Nevertheless, the framework built up from the GaS_4 tetrahedra and their connection modes (corner and edge-sharing) is quite different in the two phases.

The intensities of photoluminescence from Mn^{2+} and Ce^{3+} in the X -phase were about four and eight times higher than those in the orthorhombic phase. These emission peaks shifted toward the high energy side in comparison with those in the orthorhombic phase. Mn^{2+} and Ce^{3+} ions are known to be very sensitive with respect to the crystal field (Peters &

Baglio, 1972; Provenzano & White, 1991; Barthou *et al.*, 1994; Wang *et al.*, 2003). Thus the observed shifts of the emission peaks are assumed to be caused by a weakened crystal field originating from the decrease in the coordination number of the Ca sites in the *X*-phase.

Experimental

A mixture of CaS (4 N) and Ga₂S₃ (6 N) was used as a starting material added with a small amount of a rare earth element (REE) or a transition metal (TM) as an activator. It was weighed to 0.5 g in total according to the formula Ca_{1-x}M_xGa₂S₄ (*M* = REE or TM) (Boitier *et al.*, 2009; Obonai *et al.*, 2009). The mixture was carefully stirred to be homogenized under Ar atmosphere, and then sealed in a silica glass capsule under vacuum of 10⁻⁴ Pa, where the inner surface of the capsule was coated with a carbon film to prevent the reaction between the starting materials and the container. It was sintered at 1411 K for 1 h. The *X*-phase samples were sometimes and unexpectedly synthesized and the detailed condition how and when the *X*-phase emerges has not been clarified yet.

Refinement

Freeing of the site occupation factors for the metal and the sulfur atoms revealed no noticeable incorporation of the dopant metals or of vacancies at the S positions. The highest difference peak of 2.64 e Å⁻³ is located 1.40 Å from the Ga4 atom; the deepest hole (-3.11 e Å⁻³) is 1.39 Å from the Ga4 atom.

Computing details

Data collection: *CrystalClear* (Rigaku/MSD and Rigaku, 2006); cell refinement: *CrystalClear* (Rigaku/MSD and Rigaku, 2006); data reduction: *CrystalStructure* (Rigaku/MSD and Rigaku, 2006); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *VESTA 3* (Momma & Izumi, 2011); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSD and Rigaku, 2006).

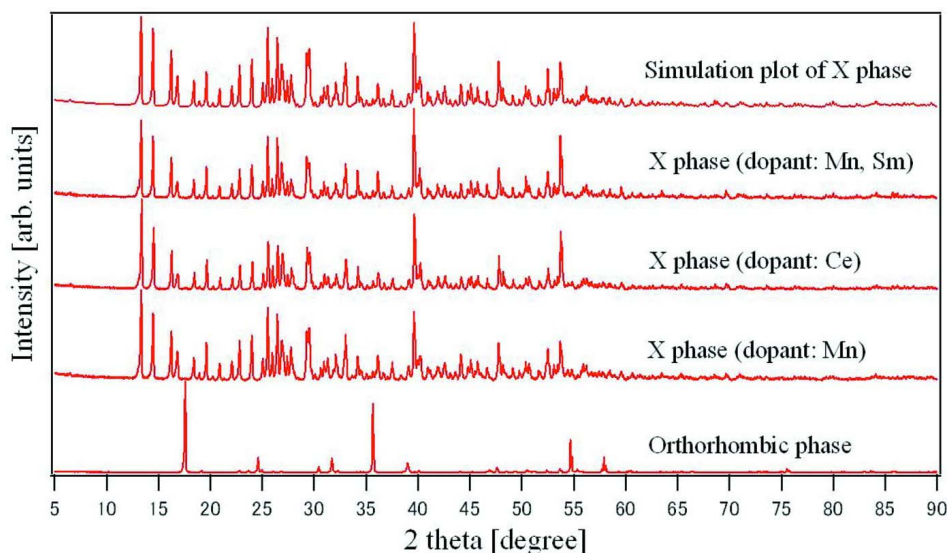


Figure 1

Experimental and simulated X-ray powder diffraction patterns of the *X*-phase of CaGa₂S₄ together with the known orthorhombic form for comparison.

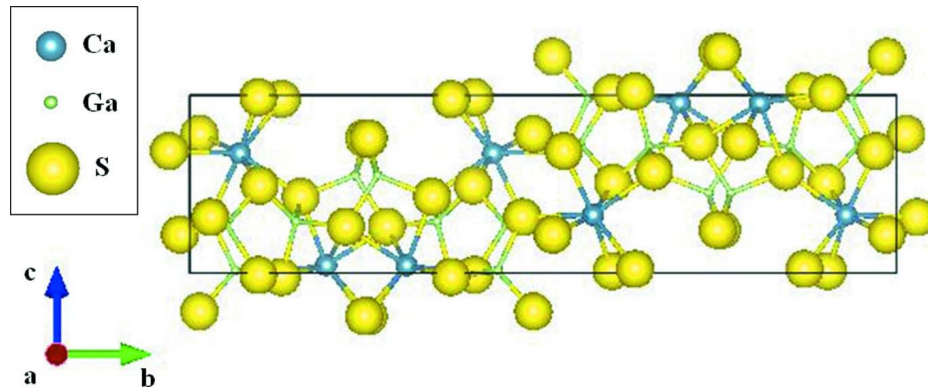


Figure 2

The unit cell of the *X*-phase of CaGa_2S_4 viewed along $[100]$.

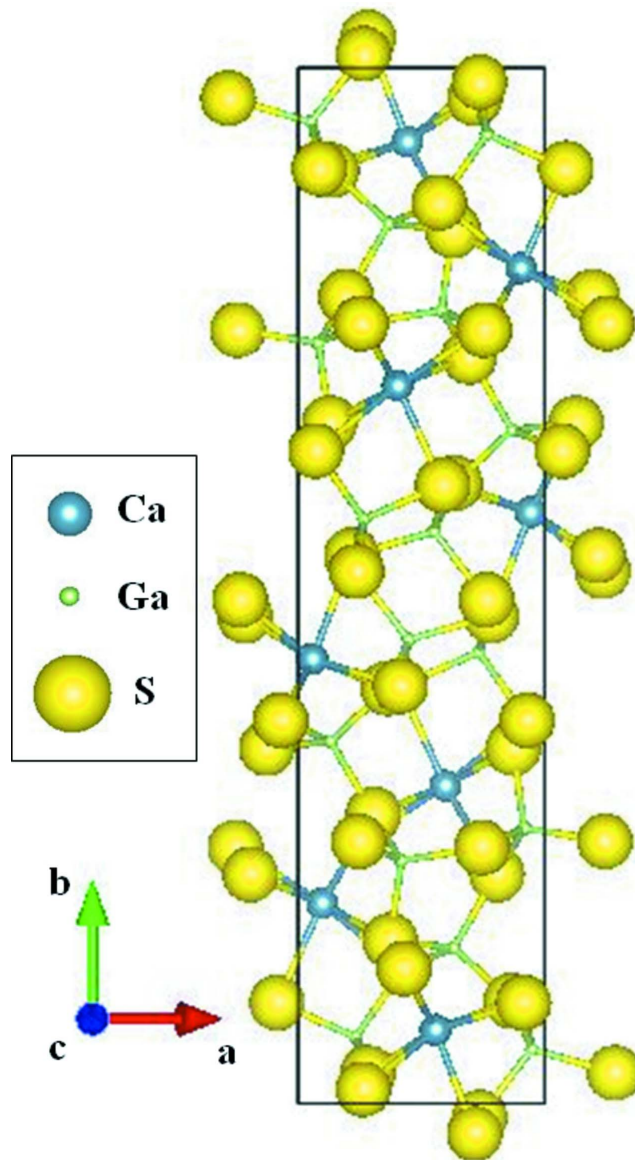
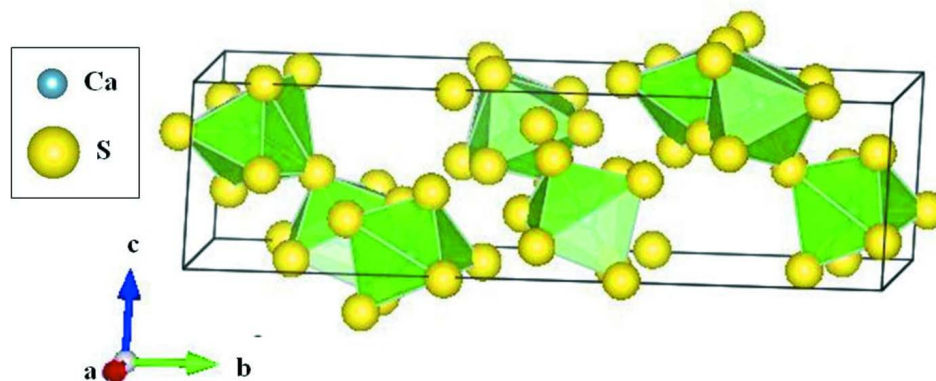
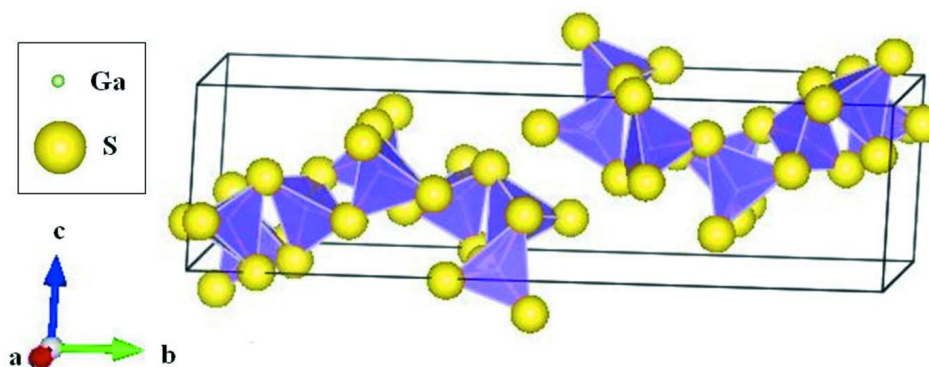


Figure 3

The unit cell of the *X*-phase of CaGa_2S_4 viewed along $[001]$.


Figure 4

The environment of the cation sites in the *X*-phase: Ca sites.


Figure 5

The environment of the cation sites in the *X*-phase: Ga sites.

calcium tetrathiodigallate(III)

Crystal data

CaGa_2S_4

$M_r = 307.76$

Monoclinic, $P2_1/a$

Hall symbol: $-P\ 2yab$

$a = 6.841(3)\ \text{\AA}$

$b = 27.069(9)\ \text{\AA}$

$c = 7.231(3)\ \text{\AA}$

$\beta = 109.413(5)^\circ$

$V = 1262.9(8)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1168.00$

$D_x = 3.237\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71075\ \text{\AA}$

Cell parameters from 3521 reflections

$\theta = 3.2\text{--}27.5^\circ$

$\mu = 10.52\ \text{mm}^{-1}$

$T = 270\ \text{K}$

Block, colorless

$0.10 \times 0.10 \times 0.05\ \text{mm}$

Data collection

Rigaku Saturn724+
diffractometer

Graphite monochromator

Detector resolution: $7.31\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan
(*REQABS*; Jacobson, 1998)

$T_{\min} = 0.417$, $T_{\max} = 0.591$

8869 measured reflections

2869 independent reflections

256 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.047$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -8 \rightarrow 6$

$k = -35 \rightarrow 26$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.050$
 $S = 1.21$
 2869 reflections
 127 parameters
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Chebychev polynomial with 3 parameters
 (Carruthers & Watkin, 1979) 6334.0000
 8721.6900 0.0000
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 2.64 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -3.10 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. ENTER SPECIAL DETAILS OF THE MOLECULAR GEOMETRY

Refinement. Refinement was performed using reflections with $F^2 > 2.0 \sigma(F^2)$. The weighted R -factor (wR) and goodness of fit (S) are based on F^2 . R -factor (gt) are based on F . The threshold expression of $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R -factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ga1	0.41763 (6)	0.234320 (10)	0.54983 (6)	0.01027 (10)
Ga2	0.63163 (6)	0.150170 (10)	0.29040 (6)	0.01047 (10)
Ga3	-0.05236 (6)	0.052250 (10)	0.27118 (6)	0.01054 (10)
Ga4	0.23350 (6)	0.064220 (10)	0.01510 (6)	0.01095 (10)
Ca1	-0.44242 (12)	0.07086 (3)	-0.32662 (11)	0.0133 (2)
Ca2	0.09658 (12)	0.19323 (3)	0.04330 (11)	0.0145 (2)
S1	-0.08531 (14)	0.09720 (3)	-0.01062 (13)	0.0114 (2)
S2	-0.13487 (14)	0.09906 (4)	0.49207 (13)	0.0125 (2)
S3	0.24485 (13)	0.25319 (4)	0.75754 (13)	0.0128 (2)
S4	0.37219 (14)	0.15701 (3)	0.42780 (13)	0.0115 (2)
S5	0.28330 (14)	0.02921 (3)	0.31401 (13)	0.0112 (2)
S6	0.30654 (14)	0.27904 (3)	0.26168 (13)	0.0114 (2)
S7	-0.26440 (15)	-0.01372 (4)	0.21648 (14)	0.0157 (2)
S8	0.42875 (14)	0.13001 (3)	-0.02150 (13)	0.0118 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ga1	0.0099 (2)	0.0137 (2)	0.0084 (2)	0.00054 (16)	0.00453 (16)	-0.00112 (16)
Ga2	0.0109 (2)	0.0120 (2)	0.0094 (2)	0.00015 (16)	0.00450 (16)	-0.00010 (16)
Ga3	0.0111 (2)	0.0126 (2)	0.0100 (2)	0.00015 (16)	0.00645 (16)	-0.00067 (16)
Ga4	0.0114 (2)	0.0141 (2)	0.0091 (2)	-0.00123 (17)	0.00581 (16)	-0.00087 (16)
Ca1	0.0127 (4)	0.0164 (4)	0.0114 (3)	-0.0016 (3)	0.0049 (3)	0.0007 (3)
Ca2	0.0146 (4)	0.0145 (4)	0.0140 (4)	-0.0003 (3)	0.0044 (3)	-0.0005 (3)
S1	0.0106 (4)	0.0161 (4)	0.0078 (4)	0.0007 (3)	0.0037 (3)	0.0016 (3)
S2	0.0153 (4)	0.0151 (5)	0.0084 (4)	0.0037 (3)	0.0056 (3)	-0.0004 (3)
S3	0.0074 (4)	0.0234 (5)	0.0088 (4)	0.0017 (3)	0.0043 (3)	-0.0004 (3)
S4	0.0134 (4)	0.0118 (4)	0.0114 (4)	-0.0002 (3)	0.0069 (3)	-0.0008 (3)

S5	0.0118 (4)	0.0151 (4)	0.0070 (4)	0.0024 (3)	0.0035 (3)	0.0015 (3)
S6	0.0135 (5)	0.0130 (4)	0.0094 (4)	0.0015 (3)	0.0062 (3)	0.0006 (3)
S7	0.0197 (5)	0.0167 (5)	0.0168 (5)	-0.0072 (3)	0.0142 (4)	-0.0073 (3)
S8	0.0124 (4)	0.0145 (4)	0.0093 (4)	-0.0029 (3)	0.0049 (3)	-0.0019 (3)

Geometric parameters (Å, °)

Ga1—S3	2.2569 (11)	Ga4—S8	2.2936 (9)
Ga1—S3 ⁱ	2.2685 (8)	Ca1—S1	2.8261 (10)
Ga1—S4	2.2522 (8)	Ca1—S2 ^{iv}	2.9260 (14)
Ga1—S6	2.3090 (9)	Ca1—S4 ^v	2.9500 (11)
Ga2—S2 ⁱⁱ	2.2458 (9)	Ca1—S5 ^v	2.8814 (10)
Ga2—S4	2.3116 (11)	Ca1—S5 ⁱⁱⁱ	2.9095 (11)
Ga2—S6 ⁱ	2.3048 (9)	Ca1—S7 ^{vi}	2.8480 (14)
Ga2—S8	2.2868 (8)	Ca1—S8 ^{vii}	3.0823 (13)
Ga3—S1	2.3190 (10)	Ca2—S1	2.8522 (11)
Ga3—S2	2.2526 (11)	Ca2—S3 ^{iv}	3.0538 (13)
Ga3—S5	2.2989 (10)	Ca2—S3 ^{viii}	2.9762 (10)
Ga3—S7	2.2513 (10)	Ca2—S4	2.9599 (10)
Ga4—S1	2.3062 (10)	Ca2—S6	2.9059 (11)
Ga4—S5	2.2795 (10)	Ca2—S6 ^{ix}	3.0127 (14)
Ga4—S7 ⁱⁱⁱ	2.2254 (11)	Ca2—S8	3.0033 (13)
S5...S7 ^x	3.4654 (14)	S7...S5 ^x	3.4654 (14)
S3—Ga1—S3 ⁱ	98.37 (3)	S3 ^{iv} —Ca2—S6 ^{ix}	130.31 (3)
S3—Ga1—S4	115.87 (4)	S3 ^{iv} —Ca2—S8	76.03 (3)
S3—Ga1—S6	113.19 (3)	S3 ^{viii} —Ca2—S4	158.30 (4)
S3 ⁱ —Ga1—S4	112.04 (3)	S3 ^{viii} —Ca2—S6	97.31 (3)
S3 ⁱ —Ga1—S6	118.40 (3)	S3 ^{viii} —Ca2—S6 ^{ix}	73.81 (3)
S4—Ga1—S6	99.93 (3)	S3 ^{viii} —Ca2—S8	130.42 (3)
S2 ⁱⁱ —Ga2—S4	104.61 (3)	S4—Ca2—S6	73.08 (2)
S2 ⁱⁱ —Ga2—S6 ⁱ	106.99 (3)	S4—Ca2—S6 ^{ix}	85.13 (3)
S2 ⁱⁱ —Ga2—S8	124.12 (3)	S4—Ca2—S8	71.28 (3)
S4—Ga2—S6 ⁱ	117.90 (3)	S6—Ca2—S6 ^{ix}	78.97 (3)
S4—Ga2—S8	98.16 (3)	S6—Ca2—S8	106.10 (3)
S6 ⁱ —Ga2—S8	105.82 (3)	S6 ^{ix} —Ca2—S8	152.63 (3)
S1—Ga3—S2	110.72 (3)	Ga3—S1—Ga4	85.00 (3)
S1—Ga3—S5	93.54 (3)	Ga3—S1—Ca1	112.55 (3)
S1—Ga3—S7	113.14 (3)	Ga3—S1—Ca2	116.58 (3)
S2—Ga3—S5	122.11 (3)	Ga4—S1—Ca1	120.51 (4)
S2—Ga3—S7	105.79 (4)	Ga4—S1—Ca2	89.07 (3)
S5—Ga3—S7	111.40 (3)	Ca1—S1—Ca2	124.13 (3)
S1—Ga4—S5	94.40 (3)	Ga2 ^{vii} —S2—Ga3	100.25 (3)
S1—Ga4—S7 ⁱⁱⁱ	120.06 (3)	Ga2 ^{vii} —S2—Ca1 ^{xi}	89.39 (3)
S1—Ga4—S8	105.16 (3)	Ga3—S2—Ca1 ^{xi}	123.91 (4)
S5—Ga4—S7 ⁱⁱⁱ	115.87 (3)	Ga1—S3—Ga1 ^{ix}	102.30 (3)
S5—Ga4—S8	121.53 (3)	Ga1—S3—Ca2 ^{xi}	134.04 (4)
S7 ⁱⁱⁱ —Ga4—S8	100.69 (4)	Ga1—S3—Ca2 ^{xii}	95.21 (3)
S1—Ca1—S2 ^{iv}	74.89 (3)	Ga1 ^{ix} —S3—Ca2 ^{xi}	92.90 (3)

S1—Ca1—S4 ^v	111.74 (3)	Ga1 ^{ix} —S3—Ca2 ^{xii}	141.19 (4)
S1—Ca1—S5 ^v	163.07 (4)	Ca2 ^{xi} —S3—Ca2 ^{xii}	99.38 (3)
S1—Ca1—S5 ⁱⁱⁱ	89.75 (3)	Ga1—S4—Ga2	102.54 (3)
S1—Ca1—S7 ^{vi}	114.26 (3)	Ga1—S4—Ca1 ^{xiii}	121.53 (3)
S1—Ca1—S8 ^{vii}	70.50 (3)	Ga1—S4—Ca2	91.27 (3)
S2 ^{iv} —Ca1—S4 ^v	75.72 (3)	Ga2—S4—Ca1 ^{xiii}	87.56 (3)
S2 ^{iv} —Ca1—S5 ^v	92.74 (3)	Ga2—S4—Ca2	87.89 (3)
S2 ^{iv} —Ca1—S5 ⁱⁱⁱ	86.54 (3)	Ca1 ^{xiii} —S4—Ca2	147.08 (3)
S2 ^{iv} —Ca1—S7 ^{vi}	160.92 (4)	Ga3—S5—Ga4	86.08 (3)
S2 ^{iv} —Ca1—S8 ^{vii}	127.19 (3)	Ga3—S5—Ca1 ^{xiii}	109.71 (4)
S4 ^v —Ca1—S5 ^v	75.27 (2)	Ga3—S5—Ca1 ⁱⁱⁱ	127.11 (3)
S4 ^v —Ca1—S5 ⁱⁱⁱ	146.76 (4)	Ga4—S5—Ca1 ^{xiii}	122.66 (3)
S4 ^v —Ca1—S7 ^{vi}	113.32 (3)	Ga4—S5—Ca1 ⁱⁱⁱ	110.69 (4)
S4 ^v —Ca1—S8 ^{vii}	81.50 (3)	Ca1 ^{xiii} —S5—Ca1 ⁱⁱⁱ	102.20 (3)
S5 ^v —Ca1—S5 ⁱⁱⁱ	77.80 (3)	Ga1—S6—Ga2 ^{ix}	112.31 (4)
S5 ^v —Ca1—S7 ^{vi}	74.43 (3)	Ga1—S6—Ca2	91.50 (3)
S5 ^v —Ca1—S8 ^{vii}	126.39 (3)	Ga1—S6—Ca2 ⁱ	121.80 (3)
S5 ⁱⁱⁱ —Ca1—S7 ^{vi}	77.09 (3)	Ga2 ^{ix} —S6—Ca2	122.40 (3)
S5 ⁱⁱⁱ —Ca1—S8 ^{vii}	130.86 (3)	Ga2 ^{ix} —S6—Ca2 ⁱ	106.99 (3)
S7 ^{vi} —Ca1—S8 ^{vii}	71.73 (3)	Ca2—S6—Ca2 ⁱ	101.95 (3)
S1—Ca2—S3 ^{iv}	128.30 (3)	Ga3—S7—Ga4 ⁱⁱⁱ	113.74 (5)
S1—Ca2—S3 ^{viii}	97.70 (3)	Ga3—S7—Ca1 ^{vi}	148.67 (5)
S1—Ca2—S4	86.52 (3)	Ga4 ⁱⁱⁱ —S7—Ca1 ^{vi}	97.39 (4)
S1—Ca2—S6	156.52 (4)	Ga2—S8—Ga4	104.91 (4)
S1—Ca2—S6 ^{ix}	88.01 (3)	Ga2—S8—Ca1 ⁱⁱ	127.28 (3)
S1—Ca2—S8	77.16 (3)	Ga2—S8—Ca2	87.30 (3)
S3 ^{iv} —Ca2—S3 ^{viii}	69.21 (3)	Ga4—S8—Ca1 ⁱⁱ	89.73 (3)
S3 ^{iv} —Ca2—S4	124.09 (3)	Ga4—S8—Ca2	85.67 (3)
S3 ^{iv} —Ca2—S6	74.18 (3)	Ca1 ⁱⁱ —S8—Ca2	144.97 (3)
S3—Ga1—S3 ⁱ —Ga1 ⁱ	−153.70 (4)	S5 ^v —Ca1—S2 ^{iv} —Ga3 ^{iv}	−38.96 (4)
S3—Ga1—S3 ⁱ —Ca2 ^{xii}	−17.36 (4)	S2 ^{iv} —Ca1—S5 ⁱⁱⁱ —Ga3 ⁱⁱⁱ	33.05 (5)
S3 ⁱ —Ga1—S3—Ga1 ^{ix}	163.03 (4)	S2 ^{iv} —Ca1—S5 ⁱⁱⁱ —Ga4 ⁱⁱⁱ	134.24 (3)
S3 ⁱ —Ga1—S3—Ca2 ^{xi}	−90.54 (5)	S5 ⁱⁱⁱ —Ca1—S2 ^{iv} —Ga3 ^{iv}	38.63 (4)
S3 ⁱ —Ga1—S3—Ca2 ^{xii}	17.88 (4)	S2 ^{iv} —Ca1—S7 ^{vi} —Ga3 ^{vi}	−17.88 (16)
S3—Ga1—S4—Ga2	−167.10 (3)	S7 ^{vi} —Ca1—S2 ^{iv} —Ga3 ^{iv}	7.90 (13)
S3—Ga1—S4—Ca2	104.78 (3)	S2 ^{iv} —Ca1—S8 ^{vii} —Ga2 ^{vii}	−64.03 (6)
S3—Ga1—S4—Ca1 ^{xiii}	−72.20 (5)	S2 ^{iv} —Ca1—S8 ^{vii} —Ga4 ^{vii}	−172.68 (3)
S4—Ga1—S3—Ga1 ^{ix}	−77.44 (4)	S2 ^{iv} —Ca1—S8 ^{vii} —Ca2 ^{vii}	105.26 (6)
S4—Ga1—S3—Ca2 ^{xi}	28.99 (5)	S8 ^{vii} —Ca1—S2 ^{iv} —Ga3 ^{iv}	179.61 (3)
S4—Ga1—S3—Ca2 ^{xii}	137.40 (3)	S4 ^v —Ca1—S5 ^v —Ga3 ^v	−62.52 (4)
S3—Ga1—S6—Ca2	−106.34 (3)	S4 ^v —Ca1—S5 ^v —Ga4 ^v	35.72 (5)
S3—Ga1—S6—Ga2 ^{ix}	19.83 (5)	S5 ^v —Ca1—S4 ^v —Ga1 ^v	170.74 (5)
S3—Ga1—S6—Ca2 ⁱ	148.59 (4)	S5 ^v —Ca1—S4 ^v —Ga2 ^v	−86.03 (3)
S6—Ga1—S3—Ga1 ^{ix}	37.16 (5)	S5 ^v —Ca1—S4 ^v —Ca2 ^v	−3.70 (8)
S6—Ga1—S3—Ca2 ^{xi}	143.58 (4)	S4 ^v —Ca1—S5 ⁱⁱⁱ —Ga3 ⁱⁱⁱ	90.16 (7)
S6—Ga1—S3—Ca2 ^{xii}	−108.00 (3)	S4 ^v —Ca1—S5 ⁱⁱⁱ —Ga4 ⁱⁱⁱ	−168.64 (6)
S3 ⁱ —Ga1—S4—Ga2	−55.34 (4)	S5 ⁱⁱⁱ —Ca1—S4 ^v —Ga1 ^v	−152.37 (6)
S3 ⁱ —Ga1—S4—Ca2	−143.46 (3)	S5 ⁱⁱⁱ —Ca1—S4 ^v —Ga2 ^v	−49.14 (7)

S3 ⁱ —Ga1—S4—Ca1 ^{xiii}	39.56 (6)	S5 ⁱⁱⁱ —Ca1—S4 ^v —Ca2 ^v	33.19 (13)
S4—Ga1—S3 ⁱ —Ga1 ⁱ	83.93 (5)	S4 ^v —Ca1—S7 ^{vi} —Ga3 ^{vi}	97.24 (8)
S4—Ga1—S3 ⁱ —Ca2 ^{xii}	-139.73 (3)	S7 ^{vi} —Ca1—S4 ^v —Ga1 ^v	105.29 (5)
S3 ⁱ —Ga1—S6—Ca2	139.35 (4)	S7 ^{vi} —Ca1—S4 ^v —Ga2 ^v	-151.48 (3)
S3 ⁱ —Ga1—S6—Ga2 ^{ix}	-94.47 (5)	S7 ^{vi} —Ca1—S4 ^v —Ca2 ^v	-69.15 (9)
S3 ⁱ —Ga1—S6—Ca2 ⁱ	34.28 (5)	S4 ^v —Ca1—S8 ^{vii} —Ga2 ^{vii}	-128.79 (4)
S6—Ga1—S3 ⁱ —Ga1 ⁱ	-31.56 (5)	S4 ^v —Ca1—S8 ^{vii} —Ga4 ^{vii}	122.55 (3)
S6—Ga1—S3 ⁱ —Ca2 ^{xii}	104.78 (4)	S4 ^v —Ca1—S8 ^{vii} —Ca2 ^{vii}	40.50 (7)
S4—Ga1—S6—Ca2	17.50 (4)	S8 ^{vii} —Ca1—S4 ^v —Ga1 ^v	39.47 (5)
S4—Ga1—S6—Ga2 ^{ix}	143.67 (4)	S8 ^{vii} —Ca1—S4 ^v —Ga2 ^v	142.70 (3)
S4—Ga1—S6—Ca2 ⁱ	-87.57 (4)	S8 ^{vii} —Ca1—S4 ^v —Ca2 ^v	-134.97 (8)
S6—Ga1—S4—Ga2	70.95 (3)	S5 ^v —Ca1—S5 ⁱⁱⁱ —Ga3 ⁱⁱⁱ	126.60 (5)
S6—Ga1—S4—Ca2	-17.17 (4)	S5 ^v —Ca1—S5 ⁱⁱⁱ —Ga4 ⁱⁱⁱ	-132.21 (4)
S6—Ga1—S4—Ca1 ^{xiii}	165.85 (4)	S5 ⁱⁱⁱ —Ca1—S5 ^v —Ga3 ^v	137.15 (4)
S2 ⁱⁱ —Ga2—S4—Ga1	107.72 (3)	S5 ⁱⁱⁱ —Ca1—S5 ^v —Ga4 ^v	-124.60 (5)
S2 ⁱⁱ —Ga2—S4—Ca2	-161.45 (3)	S5 ^v —Ca1—S7 ^{vi} —Ga3 ^{vi}	31.29 (8)
S2 ⁱⁱ —Ga2—S4—Ca1 ^{xiii}	-14.07 (3)	S7 ^{vi} —Ca1—S5 ^v —Ga3 ^v	57.35 (4)
S4—Ga2—S2 ⁱⁱ —Ga3 ⁱⁱ	138.58 (3)	S7 ^{vi} —Ca1—S5 ^v —Ga4 ^v	155.60 (5)
S2 ⁱⁱ —Ga2—S6 ⁱ —Ga1 ⁱ	-68.55 (5)	S5 ^v —Ca1—S8 ^{vii} —Ga2 ^{vii}	166.65 (4)
S2 ⁱⁱ —Ga2—S6 ⁱ —Ca2 ⁱ	-175.65 (4)	S5 ^v —Ca1—S8 ^{vii} —Ga4 ^{vii}	58.00 (4)
S6 ⁱ —Ga2—S2 ⁱⁱ —Ga3 ⁱⁱ	-95.60 (4)	S5 ^v —Ca1—S8 ^{vii} —Ca2 ^{vii}	-24.06 (9)
S2 ⁱⁱ —Ga2—S8—Ga4	61.50 (6)	S8 ^{vii} —Ca1—S5 ^v —Ga3 ^v	4.92 (6)
S2 ⁱⁱ —Ga2—S8—Ca2	146.29 (4)	S8 ^{vii} —Ca1—S5 ^v —Ga4 ^v	103.16 (5)
S2 ⁱⁱ —Ga2—S8—Ca1 ⁱⁱ	-39.84 (7)	S5 ⁱⁱⁱ —Ca1—S7 ^{vi} —Ga3 ^{vi}	-49.43 (8)
S8—Ga2—S2 ⁱⁱ —Ga3 ⁱⁱ	27.86 (6)	S7 ^{vi} —Ca1—S5 ⁱⁱⁱ —Ga3 ⁱⁱⁱ	-156.82 (5)
S4—Ga2—S6 ⁱ —Ga1 ⁱ	48.85 (4)	S7 ^{vi} —Ca1—S5 ⁱⁱⁱ —Ga4 ⁱⁱⁱ	-55.63 (3)
S4—Ga2—S6 ⁱ —Ca2 ⁱ	-58.25 (5)	S5 ⁱⁱⁱ —Ca1—S8 ^{vii} —Ga2 ^{vii}	59.76 (6)
S6 ⁱ —Ga2—S4—Ga1	-10.94 (4)	S5 ⁱⁱⁱ —Ca1—S8 ^{vii} —Ga4 ^{vii}	-48.89 (4)
S6 ⁱ —Ga2—S4—Ca2	79.88 (3)	S5 ⁱⁱⁱ —Ca1—S8 ^{vii} —Ca2 ^{vii}	-130.95 (6)
S6 ⁱ —Ga2—S4—Ca1 ^{xiii}	-132.73 (3)	S8 ^{vii} —Ca1—S5 ⁱⁱⁱ —Ga3 ⁱⁱⁱ	-105.41 (6)
S4—Ga2—S8—Ga4	-52.39 (4)	S8 ^{vii} —Ca1—S5 ⁱⁱⁱ —Ga4 ⁱⁱⁱ	-4.21 (6)
S4—Ga2—S8—Ca2	32.40 (3)	S7 ^{vi} —Ca1—S8 ^{vii} —Ga2 ^{vii}	113.12 (4)
S4—Ga2—S8—Ca1 ⁱⁱ	-153.73 (4)	S7 ^{vi} —Ca1—S8 ^{vii} —Ga4 ^{vii}	4.47 (2)
S8—Ga2—S4—Ga1	-123.75 (3)	S7 ^{vi} —Ca1—S8 ^{vii} —Ca2 ^{vii}	-77.59 (6)
S8—Ga2—S4—Ca2	-32.92 (3)	S8 ^{vii} —Ca1—S7 ^{vi} —Ga3 ^{vi}	169.08 (8)
S8—Ga2—S4—Ca1 ^{xiii}	114.47 (2)	S1—Ca2—S3 ^{iv} —Ga1 ^{iv}	-40.82 (6)
S6 ⁱ —Ga2—S8—Ga4	-174.53 (3)	S3 ^{iv} —Ca2—S1—Ga3	155.55 (4)
S6 ⁱ —Ga2—S8—Ca2	-89.74 (3)	S3 ^{iv} —Ca2—S1—Ga4	71.61 (4)
S6 ⁱ —Ga2—S8—Ca1 ⁱⁱ	84.13 (5)	S3 ^{iv} —Ca2—S1—Ca1	-55.44 (7)
S8—Ga2—S6 ⁱ —Ga1 ⁱ	157.33 (3)	S1—Ca2—S3 ^{viii} —Ga1 ^{viii}	-114.19 (4)
S8—Ga2—S6 ⁱ —Ca2 ⁱ	50.23 (5)	S1—Ca2—S3 ^{viii} —Ca2 ^{ix}	109.55 (4)
S1—Ga3—S2—Ga2 ^{vii}	30.00 (4)	S3 ^{viii} —Ca2—S1—Ga3	-134.92 (4)
S1—Ga3—S2—Ca1 ^{xi}	126.23 (4)	S3 ^{viii} —Ca2—S1—Ga4	141.13 (3)
S2—Ga3—S1—Ga4	133.76 (3)	S3 ^{viii} —Ca2—S1—Ca1	14.08 (6)
S2—Ga3—S1—Ca1	-105.20 (4)	S1—Ca2—S4—Ga1	-154.26 (4)
S2—Ga3—S1—Ca2	47.31 (5)	S1—Ca2—S4—Ga2	103.24 (3)
S1—Ga3—S5—Ga4	-7.49 (3)	S1—Ca2—S4—Ca1 ^{xiii}	21.00 (9)
S1—Ga3—S5—Ca1 ^{xiii}	115.89 (3)	S4—Ca2—S1—Ga3	23.68 (4)
S1—Ga3—S5—Ca1 ⁱⁱⁱ	-120.58 (4)	S4—Ca2—S1—Ga4	-60.26 (3)

S5—Ga3—S1—Ga4	7.41 (3)	S4—Ca2—S1—Ca1	172.69 (5)
S5—Ga3—S1—Ca1	128.44 (4)	S1—Ca2—S6—Ga1	17.08 (11)
S5—Ga3—S1—Ca2	-79.04 (4)	S1—Ca2—S6—Ga2 ^{ix}	-100.72 (10)
S1—Ga3—S7—Ga4 ⁱⁱⁱ	54.29 (5)	S1—Ca2—S6—Ca2 ⁱ	140.07 (9)
S1—Ga3—S7—Ca1 ^{vi}	-132.51 (7)	S6—Ca2—S1—Ga3	-5.63 (13)
S7—Ga3—S1—Ga4	-107.68 (3)	S6—Ca2—S1—Ga4	-89.57 (10)
S7—Ga3—S1—Ca1	13.35 (5)	S6—Ca2—S1—Ca1	143.38 (8)
S7—Ga3—S1—Ca2	165.87 (4)	S1—Ca2—S6 ^{ix} —Ga1 ^{ix}	136.61 (3)
S2—Ga3—S5—Ga4	-124.70 (4)	S1—Ca2—S6 ^{ix} —Ca2 ^{ix}	-124.02 (3)
S2—Ga3—S5—Ca1 ^{xiii}	-1.32 (5)	S6 ^{ix} —Ca2—S1—Ga3	-61.56 (4)
S2—Ga3—S5—Ca1 ⁱⁱⁱ	122.21 (5)	S6 ^{ix} —Ca2—S1—Ga4	-145.50 (3)
S5—Ga3—S2—Ga2 ^{vii}	138.38 (3)	S6 ^{ix} —Ca2—S1—Ca1	87.45 (5)
S5—Ga3—S2—Ca1 ^{xi}	-125.39 (4)	S1—Ca2—S8—Ga2	-116.60 (3)
S2—Ga3—S7—Ga4 ⁱⁱⁱ	175.67 (3)	S1—Ca2—S8—Ga4	-11.41 (2)
S2—Ga3—S7—Ca1 ^{vi}	-11.14 (9)	S1—Ca2—S8—Ca1 ⁱⁱ	71.92 (6)
S7—Ga3—S2—Ga2 ^{vii}	-92.93 (4)	S8—Ca2—S1—Ga3	95.26 (4)
S7—Ga3—S2—Ca1 ^{xi}	3.30 (5)	S8—Ca2—S1—Ga4	11.32 (2)
S5—Ga3—S7—Ga4 ⁱⁱⁱ	-49.58 (5)	S8—Ca2—S1—Ca1	-115.73 (5)
S5—Ga3—S7—Ca1 ^{vi}	123.62 (8)	S3 ^{iv} —Ca2—S3 ^{viii} —Ga1 ^{viii}	13.97 (3)
S7—Ga3—S5—Ga4	109.08 (3)	S3 ^{iv} —Ca2—S3 ^{viii} —Ca2 ^{ix}	-122.30 (3)
S7—Ga3—S5—Ca1 ^{xiii}	-127.55 (4)	S3 ^{viii} —Ca2—S3 ^{iv} —Ga1 ^{iv}	-124.07 (5)
S7—Ga3—S5—Ca1 ⁱⁱⁱ	-4.01 (6)	S3 ^{iv} —Ca2—S4—Ga1	70.62 (5)
S1—Ga4—S5—Ga3	7.54 (3)	S3 ^{iv} —Ca2—S4—Ga2	-31.88 (4)
S1—Ga4—S5—Ca1 ^{xiii}	-103.42 (4)	S3 ^{iv} —Ca2—S4—Ca1 ^{xiii}	-114.12 (8)
S1—Ga4—S5—Ca1 ⁱⁱⁱ	135.89 (3)	S4—Ca2—S3 ^{iv} —Ga1 ^{iv}	75.36 (6)
S5—Ga4—S1—Ga3	-7.48 (3)	S3 ^{iv} —Ca2—S6—Ga1	-147.66 (3)
S5—Ga4—S1—Ca1	-120.76 (4)	S3 ^{iv} —Ca2—S6—Ga2 ^{ix}	94.54 (4)
S5—Ga4—S1—Ca2	109.31 (3)	S3 ^{iv} —Ca2—S6—Ca2 ⁱ	-24.67 (3)
S1—Ga4—S7 ⁱⁱⁱ —Ga3 ⁱⁱⁱ	-55.77 (5)	S6—Ca2—S3 ^{iv} —Ga1 ^{iv}	131.51 (4)
S7 ⁱⁱⁱ —Ga4—S1—Ga3	115.90 (4)	S3 ^{iv} —Ca2—S6 ^{ix} —Ga1 ^{ix}	-81.77 (5)
S7 ⁱⁱⁱ —Ga4—S1—Ca1	2.62 (6)	S3 ^{iv} —Ca2—S6 ^{ix} —Ca2 ^{ix}	17.60 (5)
S7 ⁱⁱⁱ —Ga4—S1—Ca2	-127.31 (4)	S6 ^{ix} —Ca2—S3 ^{iv} —Ga1 ^{iv}	-168.56 (4)
S1—Ga4—S8—Ga2	100.35 (4)	S3 ^{iv} —Ca2—S8—Ga2	108.02 (3)
S1—Ga4—S8—Ca2	14.31 (3)	S3 ^{iv} —Ca2—S8—Ga4	-146.80 (3)
S1—Ga4—S8—Ca1 ⁱⁱ	-130.93 (3)	S3 ^{iv} —Ca2—S8—Ca1 ⁱⁱ	-63.47 (6)
S8—Ga4—S1—Ga3	-131.83 (3)	S8—Ca2—S3 ^{iv} —Ga1 ^{iv}	19.95 (4)
S8—Ga4—S1—Ca1	114.88 (4)	S3 ^{viii} —Ca2—S4—Ga1	-52.14 (11)
S8—Ga4—S1—Ca2	-15.04 (3)	S3 ^{viii} —Ca2—S4—Ga2	-154.64 (10)
S5—Ga4—S7 ⁱⁱⁱ —Ga3 ⁱⁱⁱ	56.51 (5)	S3 ^{viii} —Ca2—S4—Ca1 ^{xiii}	123.12 (10)
S7 ⁱⁱⁱ —Ga4—S5—Ga3	-119.03 (3)	S4—Ca2—S3 ^{viii} —Ga1 ^{viii}	145.80 (9)
S7 ⁱⁱⁱ —Ga4—S5—Ca1 ^{xiii}	130.02 (4)	S4—Ca2—S3 ^{viii} —Ca2 ^{ix}	9.54 (12)
S7 ⁱⁱⁱ —Ga4—S5—Ca1 ⁱⁱⁱ	9.33 (5)	S3 ^{viii} —Ca2—S6—Ga1	146.44 (3)
S5—Ga4—S8—Ga2	-4.69 (5)	S3 ^{viii} —Ca2—S6—Ga2 ^{ix}	28.64 (5)
S5—Ga4—S8—Ca2	-90.73 (4)	S3 ^{viii} —Ca2—S6—Ca2 ⁱ	-90.57 (3)
S5—Ga4—S8—Ca1 ⁱⁱ	124.03 (3)	S6—Ca2—S3 ^{viii} —Ga1 ^{viii}	83.93 (4)
S8—Ga4—S5—Ga3	118.33 (3)	S6—Ca2—S3 ^{viii} —Ca2 ^{ix}	-52.34 (4)
S8—Ga4—S5—Ca1 ^{xiii}	7.37 (6)	S3 ^{viii} —Ca2—S6 ^{ix} —Ga1 ^{ix}	-124.78 (4)
S8—Ga4—S5—Ca1 ⁱⁱⁱ	-113.32 (4)	S3 ^{viii} —Ca2—S6 ^{ix} —Ca2 ^{ix}	-25.41 (3)
S7 ⁱⁱⁱ —Ga4—S8—Ga2	-134.25 (3)	S6 ^{ix} —Ca2—S3 ^{viii} —Ga1 ^{viii}	160.16 (3)

S7 ⁱⁱⁱ —Ga4—S8—Ca2	139.71 (3)	S6 ^{ix} —Ca2—S3 ^{viii} —Ca2 ^{ix}	23.89 (3)
S7 ⁱⁱⁱ —Ga4—S8—Ca1 ⁱⁱ	-5.53 (3)	S3 ^{viii} —Ca2—S8—Ga2	154.19 (4)
S8—Ga4—S7 ⁱⁱⁱ —Ga3 ⁱⁱⁱ	-170.40 (3)	S3 ^{viii} —Ca2—S8—Ga4	-100.62 (4)
S1—Ca1—S2 ^{iv} —Ga3 ^{iv}	129.31 (4)	S3 ^{viii} —Ca2—S8—Ca1 ⁱⁱ	-17.29 (9)
S2 ^{iv} —Ca1—S1—Ga3	-148.00 (4)	S8—Ca2—S3 ^{viii} —Ga1 ^{viii}	-34.53 (5)
S2 ^{iv} —Ca1—S1—Ga4	-50.23 (4)	S8—Ca2—S3 ^{viii} —Ca2 ^{ix}	-170.80 (4)
S2 ^{iv} —Ca1—S1—Ca2	61.91 (5)	S4—Ca2—S6—Ga1	-13.63 (3)
S1—Ca1—S4 ^v —Ga1 ^v	-25.51 (7)	S4—Ca2—S6—Ga2 ^{ix}	-131.43 (5)
S1—Ca1—S4 ^v —Ga2 ^v	77.72 (4)	S4—Ca2—S6—Ca2 ⁱ	109.36 (3)
S1—Ca1—S4 ^v —Ca2 ^v	160.05 (7)	S6—Ca2—S4—Ga1	13.98 (3)
S4 ^v —Ca1—S1—Ga3	144.50 (4)	S6—Ca2—S4—Ga2	-88.53 (3)
S4 ^v —Ca1—S1—Ga4	-117.73 (4)	S6—Ca2—S4—Ca1 ^{xiii}	-170.76 (8)
S4 ^v —Ca1—S1—Ca2	-5.59 (7)	S4—Ca2—S6 ^{ix} —Ga1 ^{ix}	49.94 (4)
S1—Ca1—S5 ^v —Ga3 ^v	-179.34 (12)	S4—Ca2—S6 ^{ix} —Ca2 ^{ix}	149.31 (3)
S1—Ca1—S5 ^v —Ga4 ^v	-81.09 (14)	S6 ^{ix} —Ca2—S4—Ga1	-65.96 (3)
S5 ^v —Ca1—S1—Ga3	-103.81 (14)	S6 ^{ix} —Ca2—S4—Ga2	-168.46 (3)
S5 ^v —Ca1—S1—Ga4	-6.04 (16)	S6 ^{ix} —Ca2—S4—Ca1 ^{xiii}	109.30 (8)
S5 ^v —Ca1—S1—Ca2	106.10 (13)	S4—Ca2—S8—Ga2	-25.94 (2)
S1—Ca1—S5 ⁱⁱⁱ —Ga3 ⁱⁱⁱ	-41.83 (5)	S4—Ca2—S8—Ga4	79.25 (3)
S1—Ca1—S5 ⁱⁱⁱ —Ga4 ⁱⁱⁱ	59.36 (4)	S4—Ca2—S8—Ca1 ⁱⁱ	162.58 (6)
S5 ⁱⁱⁱ —Ca1—S1—Ga3	-61.51 (4)	S8—Ca2—S4—Ga1	128.13 (3)
S5 ⁱⁱⁱ —Ca1—S1—Ga4	36.26 (5)	S8—Ca2—S4—Ga2	25.63 (2)
S5 ⁱⁱⁱ —Ca1—S1—Ca2	148.40 (5)	S8—Ca2—S4—Ca1 ^{xiii}	-56.61 (8)
S1—Ca1—S7 ^{vi} —Ga3 ^{vi}	-133.22 (7)	S6—Ca2—S6 ^{ix} —Ga1 ^{ix}	-23.74 (4)
S7 ^{vi} —Ca1—S1—Ga3	14.18 (5)	S6—Ca2—S6 ^{ix} —Ca2 ^{ix}	75.63 (3)
S7 ^{vi} —Ca1—S1—Ga4	111.95 (5)	S6 ^{ix} —Ca2—S6—Ga1	74.59 (3)
S7 ^{vi} —Ca1—S1—Ca2	-135.91 (5)	S6 ^{ix} —Ca2—S6—Ga2 ^{ix}	-43.21 (4)
S1—Ca1—S8 ^{vii} —Ga2 ^{vii}	-12.04 (4)	S6 ^{ix} —Ca2—S6—Ca2 ⁱ	-162.43 (3)
S1—Ca1—S8 ^{vii} —Ga4 ^{vii}	-120.69 (3)	S6—Ca2—S8—Ga2	39.37 (3)
S1—Ca1—S8 ^{vii} —Ca2 ^{vii}	157.25 (6)	S6—Ca2—S8—Ga4	144.56 (3)
S8 ^{vii} —Ca1—S1—Ga3	72.56 (4)	S6—Ca2—S8—Ca1 ⁱⁱ	-132.12 (6)
S8 ^{vii} —Ca1—S1—Ga4	170.33 (4)	S8—Ca2—S6—Ga1	-77.71 (4)
S8 ^{vii} —Ca1—S1—Ca2	-77.53 (5)	S8—Ca2—S6—Ga2 ^{ix}	164.48 (4)
S2 ^{iv} —Ca1—S4 ^v —Ga1 ^v	-92.49 (5)	S8—Ca2—S6—Ca2 ⁱ	45.27 (3)
S2 ^{iv} —Ca1—S4 ^v —Ga2 ^v	10.73 (2)	S6 ^{ix} —Ca2—S8—Ga2	-57.78 (7)
S2 ^{iv} —Ca1—S4 ^v —Ca2 ^v	93.07 (8)	S6 ^{ix} —Ca2—S8—Ga4	47.41 (7)
S4 ^v —Ca1—S2 ^{iv} —Ga3 ^{iv}	-113.01 (4)	S6 ^{ix} —Ca2—S8—Ca1 ⁱⁱ	130.74 (7)
S2 ^{iv} —Ca1—S5 ^v —Ga3 ^v	-136.98 (3)	S8—Ca2—S6 ^{ix} —Ga1 ^{ix}	80.03 (8)
S2 ^{iv} —Ca1—S5 ^v —Ga4 ^v	-38.74 (5)	S8—Ca2—S6 ^{ix} —Ca2 ^{ix}	179.40 (6)

Symmetry codes: (i) $x+1/2, -y+1/2, z$; (ii) $x+1, y, z$; (iii) $-x, -y, -z$; (iv) $x, y, z-1$; (v) $x-1, y, z-1$; (vi) $-x-1, -y, -z$; (vii) $x-1, y, z$; (viii) $x-1/2, -y+1/2, z-1$; (ix) $x-1/2, -y+1/2, z$; (x) $-x, -y, -z+1$; (xi) $x, y, z+1$; (xii) $x+1/2, -y+1/2, z+1$; (xiii) $x+1, y, z+1$.