

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Non-isovalent substitution in a Zintl phase with the TiNiSi type structure, $\text{CaMg}_{1-x}\text{Ag}_x\text{Ge}$ [$x = 0.13$ (3)]

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Received 31 October 2009; accepted 15 November 2009

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Ge-Mg}) = 0.0006$ Å; disorder in main residue; R factor = 0.019; wR factor = 0.041; data-to-parameter ratio = 24.6.

Single crystals of the title Ag-substituted calcium magnesium germanide, $\text{CaMg}_{1-x}\text{Ag}_x\text{Ge}$ [$x = 0.13$ (3)] were obtained from the reaction of the corresponding elements at high temperature. The compound crystallizes with the TiNiSi structure type (Pearson code *oP12*) and represents an Ag-substituted derivative of the Zintl phase CaMgGe in which a small fraction of the divalent Mg atoms have been replaced by monovalent Ag atoms. All three atoms in the asymmetric unit (Ca, Mg/Ag, Ge) occupy special positions with the same site symmetry (*m.*). Although the end member CaAgGe has been reported in an isomorphic superstructure of the same TiNiSi type, higher Ag content in solid solutions could not be achieved due to competitive formation of other, perhaps more stable, phases.

Related literature

For the KHg_2 structure type, see: Duwell & Baenziger (1955) and for the TiNiSi structure type, see: Shoemaker & Shoemaker (1965); Eisenmann *et al.* (1972); Villars & Calvert (1991). For the structural systematics and properties of the TiNiSi structure type, see: Kauzlarich (1996); Landrum *et al.* (1998). For related compounds, see: Ponou & Lidin (2008); Ponou *et al.* (2007). For atomic radii, see: Pauling (1960).

Experimental

Crystal data

| | |
|---|-----------------------------------|
| $\text{CaMg}_{0.87}\text{Ag}_{0.13}\text{Ge}$ | $V = 280.99$ (1) Å ³ |
| $M_r = 147.84$ | $Z = 4$ |
| Orthorhombic, <i>Pnma</i> | Mo $K\alpha$ radiation |
| $a = 7.5128$ (2) Å | $\mu = 13.43$ mm ⁻¹ |
| $b = 4.4573$ (1) Å | $T = 293$ K |
| $c = 8.3911$ (2) Å | $0.10 \times 0.06 \times 0.04$ mm |

Data collection

| | |
|---|---------------------------------------|
| Oxford Xcalibur3 diffractometer | 2462 measured reflections |
| Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007) | 516 independent reflections |
| $T_{\min} = 0.396$, $T_{\max} = 0.584$ | 481 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.026$ |

Refinement

| | |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.019$ | 21 parameters |
| $wR(F^2) = 0.041$ | $\Delta\rho_{\text{max}} = 0.89$ e Å ⁻³ |
| $S = 1.10$ | $\Delta\rho_{\text{min}} = -0.44$ e Å ⁻³ |
| 516 reflections | |

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Financial support from the Wenner-Gren Foundation in gratefully acknowledged. The authors thank Professor Sven Lidin (Stockholm University, Sweden) for continuous support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5206).

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supporting information

Acta Cryst. (2009). E65, i90 [doi:10.1107/S1600536809048454]

Non-isovalent substitution in a Zintl phase with the TiNiSi type structure, $\text{CaMg}_{1-x}\text{Ag}_x\text{Ge}$ [$x = 0.13$ (3)]

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S1. Comment

The solid solution $\text{CaMg}_{1-x}\text{Ag}_x\text{Ge}$ [$x = 0.13$ (3)] is iso-structural with the non-substituted ternary phase CaMgGe (Eisenmann *et al.*, 1972). It crystallizes in the TiNiSi type (Space Group *Pnma*) with Ca, Mg/Ag, and Ge at Ti, Ni, and Si positions, respectively. The TiNiSi type (Shoemaker & Shoemaker, 1965) which is well represented among ternary equiatomic phases (Villars & Calvert, 1991), is an ordered ternary derivative of the KHg_2 type (Duwell & Baenziger, 1955; Pearson code oI12). Hence, the structure consist of a three-dimensional four-connected anionic $[\text{Mg}_{1-x}\text{Ag}_x\text{Ge}]$ networks with the Ca cations sitting in large channels (Fig. 1). The anionic network may be constructed from two-dimensional sheets, similar to those in black phosphorus and running perpendicular to the *a*-axis, which are linked along the *a*-direction to form one-dimensional ladders of edge-sharing four-rings and channels of eight-rings running along the *b*-direction. The TiNiSi type is known to be very versatile and shows remarkable structural and electronic flexibility (Landrum *et al.*, 1998). Meanwhile, a large number of compounds with the TiNiSi type like CaMgGe can be rationalized as Zintl phases (Kauzlarich, 1996) according to the ionic formulation $\text{Ca}^{2+}(\text{Mg}^{2+}\text{Ge}^{4-})$. Zintl phases are known to be very sensitive to the electron count (Ponou *et al.*, 2007). But, because of the above mentioned flexibility of the TiNiSi type, non-isovalent substitutions was expected without major structural distortion. Thus, since CaAgGe crystallizes in the isomorphic (i_3) superstructure of the TiNiSi type with a tripling of the *a*-axis (Ponou & Lidin, 2008), a wide stoichiometry breadth was expected in the system $\text{CaMg}_{1-x}\text{Ag}_x\text{Ge}$. Eventually, the reaction of different starting mixtures with $x = 1/4$, $1/2$, and $3/4$, yielded almost the same composition ($x = 0.10 - 0.13$) within 3σ standard deviation. This indicates a narrow homogeneity range, meaning that in this class of materials, the inherent electronic rigidity of the Zintl phase may be conflicting with the otherwise remarkable flexibility of TiNiSi type.

$\text{CaMg}_{0.87(1)}\text{Ag}_{0.13(1)}\text{Ge}$ is the Ag-richest phase that was structurally characterized. The unit-cell volume here ($V = 280.99(1) \text{ \AA}^3$) is quite similar to that of the non-substituted phase CaMgGe ($V = 280.89 \text{ \AA}^3$), though the size of Mg is significantly larger than [Pauling's (1960) radii: Mg 1.600 Å, Ag 1.440 Å]. But, it should be noted that the later cell parameters were determined with much higher standard deviation (Eisenmann *et al.*, 1972). In a reinvestigation of the CaMgGe structure (not reported), no indications of any superstructure were found.

S2. Experimental

Three different mixtures of the elements (all from ABCR GmbH, Karlsruhe, Germany) Ca (granule, 99.5%), Mg (pieces, 99.9%), Ag (60m powder, 99.9%), and Ge (50m powder, 99.999%), with compositions along the $\text{CaMg}_{1-x}\text{Ag}_x\text{Ge}$ series with $x = 1/4$, $1/2$, and 0.75 were loaded in a Niobium ampoules (approx. 9 mm diameter and 30 mm length) which were sealed on both ends by arc-melting and, in turn, enclosed in evacuated fused silica Schlenk tube to protect the former from air oxidation at high temperature. The ampoules were heated at 1273 K for 2 h, and cooled at a rate of 6 K/h to 923 K, where they are annealed for 24 h, then cooled down to room temperature by turning off the furnace. Semi quantitative

EDX analysis of the single crystals confirmed the presence of the four elements, and no eventual contaminant at the detection limit could be observed.

S3. Refinement

The refinement was straightforward, the full occupancies for all sites were verified by freeing the site occupation factor for an individual atom, while keeping that of the other atoms fixed. This proved that all positions but one, the Mg site, were fully occupied. The refined occupancy at Mg assigned position was higher than 100%, indicating a mixing with heavier element. Therefore, this position (labelled Mg/Ag) was modelled as a statistical mixture of Mg and Ag, and refined as 86.9 (1)% Mg and 13.1 (1)% Ag.

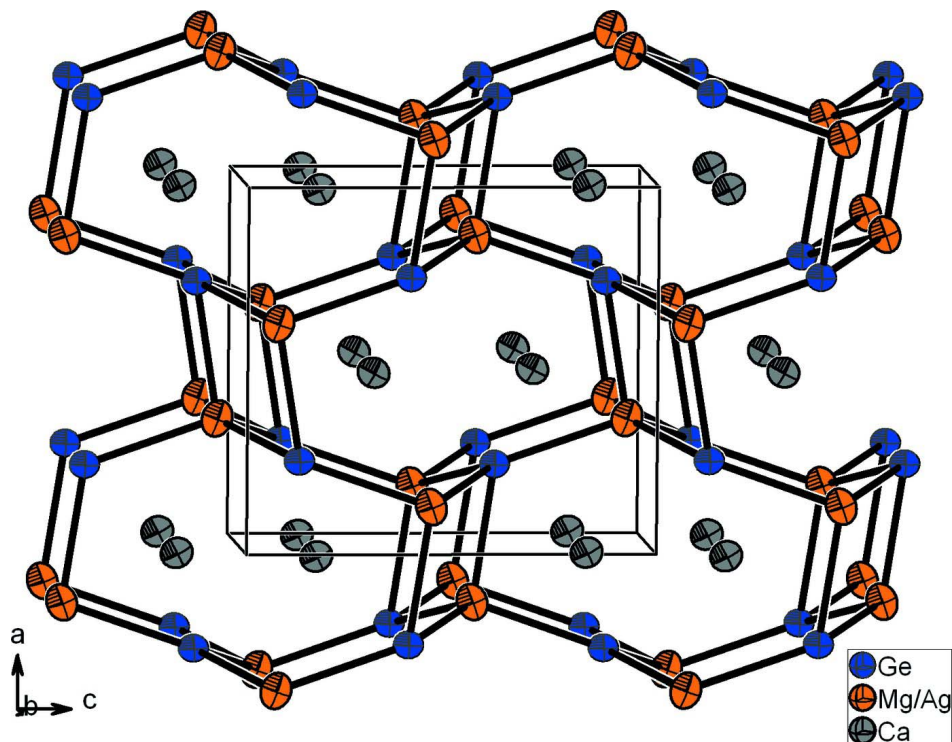


Figure 1

A perspective view of (I) with displacement ellipsoids drawn at 95% probability level. Ca, Mg/Ag, and Ge atoms are drawn as grey crossed, orange and blue spheres, respectively.

calcium magnesium silver germanide

Crystal data

$\text{CaMg}_{0.87}\text{Ag}_{0.13}\text{Ge}$

$M_r = 147.84$

Orthorhombic, $Pnma$

Hall symbol: $-P\ 2ac\ 2n$

$a = 7.5128\ (2)\ \text{\AA}$

$b = 4.4573\ (1)\ \text{\AA}$

$c = 8.3911\ (2)\ \text{\AA}$

$V = 280.99\ (1)\ \text{\AA}^3$

$Z = 4$

$F(000) = 273.5$

$D_x = 3.495\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2462 reflections

$\theta = 4.9\text{--}32.1^\circ$

$\mu = 13.43\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Irregular block, grey

$0.10 \times 0.06 \times 0.04\ \text{mm}$

Data collection

| | |
|--|--|
| Oxford Xcalibur3 diffractometer | 2462 measured reflections 516 independent reflections |
| Radiation source: Enhance (Mo) X-ray Source | 481 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{\text{int}} = 0.026$ |
| Detector resolution: 16.5467 pixels mm^{-1} | $\theta_{\text{max}} = 32.1^\circ$, $\theta_{\text{min}} = 4.6^\circ$ |
| ω scans | $h = -8 \rightarrow 10$ |
| Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007) | $k = -5 \rightarrow 6$ |
| $T_{\text{min}} = 0.396$, $T_{\text{max}} = 0.584$ | $l = -12 \rightarrow 12$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0233P)^2]$ |
| Least-squares matrix: full | where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.019$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $wR(F^2) = 0.041$ | $\Delta\rho_{\text{max}} = 0.89 \text{ e } \text{\AA}^{-3}$ |
| $S = 1.10$ | $\Delta\rho_{\text{min}} = -0.44 \text{ e } \text{\AA}^{-3}$ |
| 516 reflections | Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| 21 parameters | Extinction coefficient: 0.084 (3) |
| 0 restraints | |

Special details

Experimental. *CrysAlis RED*, (Oxford Diffraction, 2007) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|--------|-------------|----------------------------------|-------------|
| Ge1 | 0.76875 (4) | 0.2500 | 0.38457 (3) | 0.00994 (12) | |
| Ag1 | 0.14396 (8) | 0.2500 | 0.43738 (7) | 0.0140 (2) | 0.1309 (15) |
| Mg1 | 0.14396 (8) | 0.2500 | 0.43738 (7) | 0.0140 (2) | 0.8691 (15) |
| Ca1 | 0.51982 (7) | 0.2500 | 0.68206 (7) | 0.01280 (14) | |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|----------|---------------|----------|
| Ge1 | 0.00976 (16) | 0.00827 (16) | 0.01178 (17) | 0.000 | -0.00007 (9) | 0.000 |
| Ag1 | 0.0172 (4) | 0.0124 (3) | 0.0124 (3) | 0.000 | -0.0020 (2) | 0.000 |
| Mg1 | 0.0172 (4) | 0.0124 (3) | 0.0124 (3) | 0.000 | -0.0020 (2) | 0.000 |
| Ca1 | 0.0119 (3) | 0.0134 (3) | 0.0131 (3) | 0.000 | -0.00085 (18) | 0.000 |

Geometric parameters (Å, °)

| | | | |
|--|--------------|---|--------------|
| Ge1—Mg1 ⁱ | 2.7621 (4) | Ag1—Ag1 ^{viii} | 3.2788 (9) |
| Ge1—Ag1 ⁱ | 2.7621 (4) | Ag1—Mg1 ^{ix} | 3.2788 (9) |
| Ge1—Mg1 ⁱⁱ | 2.7621 (4) | Ag1—Ag1 ^{ix} | 3.2788 (9) |
| Ge1—Ag1 ⁱⁱ | 2.7621 (4) | Ag1—Ca1 ^x | 3.3267 (8) |
| Ge1—Ag1 ⁱⁱⁱ | 2.8535 (7) | Ag1—Ca1 ^{xi} | 3.3273 (6) |
| Ge1—Mg1 ⁱⁱⁱ | 2.8535 (7) | Ag1—Ca1 ^{xii} | 3.3273 (6) |
| Ge1—Mg1 ^{iv} | 2.8596 (7) | Ag1—Ca1 | 3.4912 (8) |
| Ge1—Ag1 ^{iv} | 2.8596 (7) | Ca1—Ge1 ⁱⁱ | 3.1590 (4) |
| Ge1—Ca1 | 3.1191 (6) | Ca1—Ge1 ⁱ | 3.1590 (4) |
| Ge1—Ca1 ⁱⁱ | 3.1590 (4) | Ca1—Ge1 ^{xiii} | 3.2214 (4) |
| Ge1—Ca1 ⁱ | 3.1590 (4) | Ca1—Ge1 ^{xiv} | 3.2214 (4) |
| Ge1—Ca1 ^v | 3.2214 (4) | Ca1—Mg1 ^{xv} | 3.3267 (8) |
| Ag1—Ge1 ⁱ | 2.7621 (4) | Ca1—Ag1 ^{xv} | 3.3267 (8) |
| Ag1—Ge1 ⁱⁱ | 2.7621 (4) | Ca1—Mg1 ^{xvi} | 3.3273 (6) |
| Ag1—Ge1 ^{vi} | 2.8535 (7) | Ca1—Ag1 ^{xvi} | 3.3273 (6) |
| Ag1—Ge1 ^{vii} | 2.8596 (7) | Ca1—Mg1 ^{xvii} | 3.3273 (6) |
| Ag1—Mg1 ^{viii} | 3.2788 (9) | Ca1—Ag1 ^{xvii} | 3.3273 (6) |
| Mg1 ⁱ —Ge1—Ag1 ⁱ | 0.00 (2) | Ge1 ⁱ —Ag1—Ca1 ^x | 63.086 (14) |
| Mg1 ⁱ —Ge1—Mg1 ⁱⁱ | 107.58 (2) | Ge1 ⁱⁱ —Ag1—Ca1 ^x | 63.086 (14) |
| Ag1 ⁱ —Ge1—Mg1 ⁱⁱ | 107.58 (2) | Ge1 ^{vi} —Ag1—Ca1 ^x | 82.653 (19) |
| Mg1 ⁱ —Ge1—Ag1 ⁱⁱ | 107.58 (2) | Ge1 ^{vii} —Ag1—Ca1 ^x | 177.14 (3) |
| Ag1 ⁱ —Ge1—Ag1 ⁱⁱ | 107.58 (2) | Mg1 ^{viii} —Ag1—Ca1 ^x | 60.49 (2) |
| Mg1 ⁱⁱ —Ge1—Ag1 ⁱⁱ | 0.0 | Ag1 ^{viii} —Ag1—Ca1 ^x | 60.49 (2) |
| Mg1 ⁱ —Ge1—Ag1 ⁱⁱⁱ | 71.425 (16) | Mg1 ^{ix} —Ag1—Ca1 ^x | 60.49 (2) |
| Ag1 ⁱ —Ge1—Ag1 ⁱⁱⁱ | 71.425 (16) | Ag1 ^{ix} —Ag1—Ca1 ^x | 60.49 (2) |
| Mg1 ⁱⁱ —Ge1—Ag1 ⁱⁱⁱ | 71.425 (16) | Ge1 ⁱ —Ag1—Ca1 ^{xi} | 167.565 (19) |
| Ag1 ⁱⁱ —Ge1—Ag1 ⁱⁱⁱ | 71.425 (16) | Ge1 ⁱⁱ —Ag1—Ca1 ^{xi} | 84.010 (9) |
| Mg1 ⁱ —Ge1—Mg1 ⁱⁱⁱ | 71.425 (16) | Ge1 ^{vi} —Ag1—Ca1 ^{xi} | 62.269 (13) |
| Ag1 ⁱ —Ge1—Mg1 ⁱⁱⁱ | 71.425 (16) | Ge1 ^{vii} —Ag1—Ca1 ^{xi} | 60.851 (14) |
| Mg1 ⁱⁱ —Ge1—Mg1 ⁱⁱⁱ | 71.425 (16) | Mg1 ^{viii} —Ag1—Ca1 ^{xi} | 60.470 (16) |
| Ag1 ⁱⁱ —Ge1—Mg1 ⁱⁱⁱ | 71.425 (16) | Ag1 ^{viii} —Ag1—Ca1 ^{xi} | 60.470 (16) |
| Ag1 ⁱⁱⁱ —Ge1—Mg1 ⁱⁱⁱ | 0.00 (2) | Mg1 ^{ix} —Ag1—Ca1 ^{xi} | 114.69 (3) |
| Mg1 ⁱ —Ge1—Mg1 ^{iv} | 126.076 (12) | Ag1 ^{ix} —Ag1—Ca1 ^{xi} | 114.69 (3) |
| Ag1 ⁱ —Ge1—Mg1 ^{iv} | 126.076 (12) | Ca1 ^x —Ag1—Ca1 ^{xi} | 120.958 (16) |
| Mg1 ⁱⁱ —Ge1—Mg1 ^{iv} | 126.075 (12) | Ge1 ⁱ —Ag1—Ca1 ^{xii} | 84.010 (9) |
| Ag1 ⁱⁱ —Ge1—Mg1 ^{iv} | 126.075 (12) | Ge1 ⁱⁱ —Ag1—Ca1 ^{xii} | 167.565 (19) |
| Ag1 ⁱⁱⁱ —Ge1—Mg1 ^{iv} | 118.073 (19) | Ge1 ^{vi} —Ag1—Ca1 ^{xii} | 62.269 (13) |
| Mg1 ⁱⁱⁱ —Ge1—Mg1 ^{iv} | 118.073 (19) | Ge1 ^{vii} —Ag1—Ca1 ^{xii} | 60.851 (14) |
| Mg1 ⁱ —Ge1—Ag1 ^{iv} | 126.076 (12) | Mg1 ^{viii} —Ag1—Ca1 ^{xii} | 114.69 (3) |
| Ag1 ⁱ —Ge1—Ag1 ^{iv} | 126.076 (12) | Ag1 ^{viii} —Ag1—Ca1 ^{xii} | 114.69 (3) |
| Mg1 ⁱⁱ —Ge1—Ag1 ^{iv} | 126.075 (12) | Mg1 ^{ix} —Ag1—Ca1 ^{xii} | 60.470 (16) |
| Ag1 ⁱⁱ —Ge1—Ag1 ^{iv} | 126.075 (12) | Ag1 ^{ix} —Ag1—Ca1 ^{xii} | 60.470 (16) |
| Ag1 ⁱⁱⁱ —Ge1—Ag1 ^{iv} | 118.073 (19) | Ca1 ^x —Ag1—Ca1 ^{xii} | 120.958 (16) |
| Mg1 ⁱⁱⁱ —Ge1—Ag1 ^{iv} | 118.073 (19) | Ca1 ^{xi} —Ag1—Ca1 ^{xii} | 84.104 (19) |
| Mg1 ^{iv} —Ge1—Ag1 ^{iv} | 0.00 (2) | Ge1 ⁱ —Ag1—Ca1 | 59.328 (12) |

| | | | |
|---|--------------|---|--------------|
| MgI ⁱ —GeI—CaI | 73.110 (14) | GeI ⁱⁱ —AgI—CaI | 59.328 (12) |
| AgI ⁱ —GeI—CaI | 73.110 (14) | GeI ^{vi} —AgI—CaI | 152.91 (2) |
| MgI ⁱⁱ —GeI—CaI | 73.110 (14) | GeI ^{vii} —AgI—CaI | 106.88 (2) |
| AgI ⁱⁱ —GeI—CaI | 73.110 (14) | MgI ^{viii} —AgI—CaI | 110.19 (2) |
| AgI ⁱⁱⁱ —GeI—CaI | 117.905 (19) | AgI ^{viii} —AgI—CaI | 110.19 (2) |
| MgI ⁱⁱⁱ —GeI—CaI | 117.905 (19) | MgI ^{ix} —AgI—CaI | 110.19 (2) |
| MgI ^{iv} —GeI—CaI | 124.022 (18) | AgI ^{ix} —AgI—CaI | 110.19 (2) |
| AgI ^{iv} —GeI—CaI | 124.022 (18) | CaI ^x —AgI—CaI | 70.261 (14) |
| MgI ⁱ —GeI—CaI ⁱⁱ | 145.884 (18) | CaI ^{xi} —AgI—CaI | 132.669 (11) |
| AgI ⁱ —GeI—CaI ⁱⁱ | 145.884 (18) | CaI ^{xii} —AgI—CaI | 132.669 (11) |
| MgI ⁱⁱ —GeI—CaI ⁱⁱ | 71.906 (14) | GeI—CaI—GeI ⁱⁱ | 105.655 (14) |
| AgI ⁱⁱ —GeI—CaI ⁱⁱ | 71.906 (14) | GeI—CaI—GeI ⁱ | 105.655 (14) |
| AgI ⁱⁱⁱ —GeI—CaI ⁱⁱ | 134.864 (8) | GeI ⁱⁱ —CaI—GeI ⁱ | 89.738 (15) |
| MgI ⁱⁱⁱ —GeI—CaI ⁱⁱ | 134.864 (8) | GeI—CaI—GeI ^{xiii} | 97.268 (13) |
| MgI ^{iv} —GeI—CaI ⁱⁱ | 66.910 (14) | GeI ⁱⁱ —CaI—GeI ^{xiii} | 156.90 (2) |
| AgI ^{iv} —GeI—CaI ⁱⁱ | 66.910 (14) | GeI ⁱ —CaI—GeI ^{xiii} | 86.771 (6) |
| CaI—GeI—CaI ⁱⁱ | 74.345 (14) | GeI—CaI—GeI ^{xiv} | 97.268 (13) |
| MgI ⁱ —GeI—CaI ⁱ | 71.906 (14) | GeI ⁱⁱ —CaI—GeI ^{xiv} | 86.771 (6) |
| AgI ⁱ —GeI—CaI ⁱ | 71.906 (14) | GeI ⁱ —CaI—GeI ^{xiv} | 156.90 (2) |
| MgI ⁱⁱ —GeI—CaI ⁱ | 145.884 (18) | GeI ^{xiii} —CaI—GeI ^{xiv} | 87.548 (14) |
| AgI ⁱⁱ —GeI—CaI ⁱ | 145.884 (18) | GeI—CaI—MgI ^{xv} | 126.88 (2) |
| AgI ⁱⁱⁱ —GeI—CaI ⁱ | 134.864 (8) | GeI ⁱⁱ —CaI—MgI ^{xv} | 111.240 (16) |
| MgI ⁱⁱⁱ —GeI—CaI ⁱ | 134.864 (8) | GeI ⁱ —CaI—MgI ^{xv} | 111.240 (16) |
| MgI ^{iv} —GeI—CaI ⁱ | 66.910 (14) | GeI ^{xiii} —CaI—MgI ^{xv} | 49.866 (10) |
| AgI ^{iv} —GeI—CaI ⁱ | 66.910 (14) | GeI ^{xiv} —CaI—MgI ^{xv} | 49.866 (10) |
| CaI—GeI—CaI ⁱ | 74.345 (14) | GeI—CaI—AgI ^{xv} | 126.88 (2) |
| CaI ⁱⁱ —GeI—CaI ⁱ | 89.738 (15) | GeI ⁱⁱ —CaI—AgI ^{xv} | 111.240 (16) |
| MgI ⁱ —GeI—CaI ^v | 136.591 (17) | GeI ⁱ —CaI—AgI ^{xv} | 111.240 (16) |
| AgI ⁱ —GeI—CaI ^v | 136.591 (17) | GeI ^{xiii} —CaI—AgI ^{xv} | 49.866 (10) |
| MgI ⁱⁱ —GeI—CaI ^v | 67.048 (15) | GeI ^{xiv} —CaI—AgI ^{xv} | 49.866 (10) |
| AgI ⁱⁱ —GeI—CaI ^v | 67.048 (15) | MgI ^{xv} —CaI—AgI ^{xv} | 0.000 (6) |
| AgI ⁱⁱⁱ —GeI—CaI ^v | 66.097 (13) | GeI—CaI—MgI ^{xvi} | 137.481 (10) |
| MgI ⁱⁱⁱ —GeI—CaI ^v | 66.097 (13) | GeI ⁱⁱ —CaI—MgI ^{xvi} | 109.433 (18) |
| MgI ^{iv} —GeI—CaI ^v | 70.325 (14) | GeI ⁱ —CaI—MgI ^{xvi} | 52.239 (12) |
| AgI ^{iv} —GeI—CaI ^v | 70.325 (14) | GeI ^{xiii} —CaI—MgI ^{xvi} | 51.633 (12) |
| CaI—GeI—CaI ^v | 135.874 (8) | GeI ^{xiv} —CaI—MgI ^{xvi} | 107.823 (18) |
| CaI ⁱⁱ —GeI—CaI ^v | 75.935 (6) | MgI ^{xv} —CaI—MgI ^{xvi} | 59.042 (16) |
| CaI ⁱ —GeI—CaI ^v | 137.148 (11) | AgI ^{xv} —CaI—MgI ^{xvi} | 59.042 (16) |
| GeI ⁱ —AgI—GeI ⁱⁱ | 107.58 (2) | GeI—CaI—AgI ^{xvi} | 137.481 (10) |
| GeI ⁱ —AgI—GeI ^{vi} | 108.575 (16) | GeI ⁱⁱ —CaI—AgI ^{xvi} | 109.433 (18) |
| GeI ⁱⁱ —AgI—GeI ^{vi} | 108.575 (16) | GeI ⁱ —CaI—AgI ^{xvi} | 52.239 (12) |
| GeI ⁱ —AgI—GeI ^{vii} | 115.669 (14) | GeI ^{xiii} —CaI—AgI ^{xvi} | 51.633 (12) |
| GeI ⁱⁱ —AgI—GeI ^{vii} | 115.669 (14) | GeI ^{xiv} —CaI—AgI ^{xvi} | 107.823 (18) |
| GeI ^{vi} —AgI—GeI ^{vii} | 100.20 (2) | MgI ^{xv} —CaI—AgI ^{xvi} | 59.042 (16) |
| GeI ⁱ —AgI—MgI ^{viii} | 122.12 (3) | AgI ^{xv} —CaI—AgI ^{xvi} | 59.042 (16) |
| GeI ⁱⁱ —AgI—MgI ^{viii} | 55.586 (12) | MgI ^{xvi} —CaI—AgI ^{xvi} | 0.00 (3) |
| GeI ^{vi} —AgI—MgI ^{viii} | 52.990 (18) | GeI—CaI—MgI ^{xvii} | 137.481 (10) |
| GeI ^{vii} —AgI—MgI ^{viii} | 121.27 (2) | GeI ⁱⁱ —CaI—MgI ^{xvii} | 52.239 (12) |

| | | | |
|--|-------------|--|--------------|
| Ge1 ⁱ —Ag1—Ag1 ^{viii} | 122.12 (3) | Ge1 ⁱ —Ca1—Mg1 ^{xvii} | 109.433 (18) |
| Ge1 ⁱⁱ —Ag1—Ag1 ^{viii} | 55.586 (12) | Ge1 ^{xiii} —Ca1—Mg1 ^{xvii} | 107.823 (18) |
| Ge1 ^{vi} —Ag1—Ag1 ^{viii} | 52.990 (18) | Ge1 ^{xiv} —Ca1—Mg1 ^{xvii} | 51.633 (12) |
| Ge1 ^{vii} —Ag1—Ag1 ^{viii} | 121.27 (2) | Mg1 ^{xv} —Ca1—Mg1 ^{xvii} | 59.042 (16) |
| Mg1 ^{viii} —Ag1—Ag1 ^{viii} | 0.000 (16) | Ag1 ^{xv} —Ca1—Mg1 ^{xvii} | 59.042 (16) |
| Ge1 ⁱ —Ag1—Mg1 ^{ix} | 55.586 (12) | Mg1 ^{xvi} —Ca1—Mg1 ^{xvii} | 84.104 (19) |
| Ge1 ⁱⁱ —Ag1—Mg1 ^{ix} | 122.12 (3) | Ag1 ^{xvi} —Ca1—Mg1 ^{xvii} | 84.104 (19) |
| Ge1 ^{vi} —Ag1—Mg1 ^{ix} | 52.990 (18) | Ge1—Ca1—Ag1 ^{xvii} | 137.481 (10) |
| Ge1 ^{vii} —Ag1—Mg1 ^{ix} | 121.27 (2) | Ge1 ⁱⁱ —Ca1—Ag1 ^{xvii} | 52.239 (12) |
| Mg1 ^{viii} —Ag1—Mg1 ^{ix} | 85.64 (3) | Ge1 ⁱ —Ca1—Ag1 ^{xvii} | 109.433 (18) |
| Ag1 ^{viii} —Ag1—Mg1 ^{ix} | 85.64 (3) | Ge1 ^{xiii} —Ca1—Ag1 ^{xvii} | 107.823 (18) |
| Ge1 ⁱ —Ag1—Ag1 ^{ix} | 55.586 (12) | Ge1 ^{xiv} —Ca1—Ag1 ^{xvii} | 51.633 (12) |
| Ge1 ⁱⁱ —Ag1—Ag1 ^{ix} | 122.12 (3) | Mg1 ^{xv} —Ca1—Ag1 ^{xvii} | 59.042 (16) |
| Ge1 ^{vi} —Ag1—Ag1 ^{ix} | 52.990 (18) | Ag1 ^{xv} —Ca1—Ag1 ^{xvii} | 59.042 (16) |
| Ge1 ^{vii} —Ag1—Ag1 ^{ix} | 121.27 (2) | Mg1 ^{xvi} —Ca1—Ag1 ^{xvii} | 84.104 (19) |
| Mg1 ^{viii} —Ag1—Ag1 ^{ix} | 85.64 (3) | Ag1 ^{xvi} —Ca1—Ag1 ^{xvii} | 84.104 (19) |
| Ag1 ^{viii} —Ag1—Ag1 ^{ix} | 85.64 (3) | Mg1 ^{xvii} —Ca1—Ag1 ^{xvii} | 0.00 (2) |
| Mg1 ^{ix} —Ag1—Ag1 ^{ix} | 0.000 (16) | | |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $x+1, y, z$; (iv) $x+1/2, y, -z+1/2$; (v) $-x+3/2, -y, z-1/2$; (vi) $x-1, y, z$; (vii) $x-1/2, y, -z+1/2$; (viii) $-x, -y, -z+1$; (ix) $-x, -y+1, -z+1$; (x) $x-1/2, y, -z+3/2$; (xi) $-x+1/2, -y, z-1/2$; (xii) $-x+1/2, -y+1, z-1/2$; (xiii) $-x+3/2, -y+1, z+1/2$; (xiv) $-x+3/2, -y, z+1/2$; (xv) $x+1/2, y, -z+3/2$; (xvi) $-x+1/2, -y+1, z+1/2$; (xvii) $-x+1/2, -y, z+1/2$.