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$Ca_{7.96}Cu_{0.04}Ge_5O_{18}$: a new calcium germanate with GeO_4 and Ge_3O_{10} units

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The title compound, octacalcium copper pentagermanium octadecaoxide, represents a new intermediate phase between CaO and GeO_2, and has not previously been reported in the literature. The structure consists of three different Ge sites, two of them on general 8*d* positions, site symmetry 1, one on special position 4*d*, site symmetry 2. Three of the five Ca sites occur on 8*d* positions, site symmtery 1, one Ca is on 4*b* with site symmetry $\overline{1}$ and one Ca is on 4*c* with site symmetry 2. All nine O atoms have symmetry 1 (8*d* position). By sharing common edges, the Ca sites form infinite bands parallel to the *c* axis, and these bands are interconnected by isolated GeO_4 and Ge_3O_{10} units. These (100) layers are stacked along *a* in an *ABAB*... sequence, with the *B* layer being inverted and displaced along *b*/2.

Comment

Detailed phase-equilibrium studies by Eulenberger *et al.* (1962) and Shirvinskaya *et al.* (1966) revealed the presence of six intermediate phases in the CaO–GeO_2 system. These are Ca_3GeO_5, which is metastable below 1593 K, Ca_2GeO_4, $Ca_3Ge_2O_7$, $CaGeO_3$, $CaGe_2O_5$ and $CaGe_4O_9$. Structure determinations have been performed on several of these compounds, including Ca_3GeO_5, which shows polymorphic forms including two-layer, nine-layer and 24-layer structures (Nishi & Takéuchi, 1984, 1985, 1986). A high-pressure polymorph of Ca_2GeO_4 was investigated by Reid & Ringwood (1970). $CaGeO_3$ shows a wollastonite-type structure under ambient conditions (Barbier & Levy, 1997) and two high-pressure polymorphs (Prewitt & Sleigth, 1969; Sasaki *et al.*, 1983), while $CaGe_2O_5$ is reported to have two polymorphs (Aust *et al.*, 1976, Nevsky, Ilyuskin & Belov, 1979). Additionally, Barbier & Levy (1997) report on the triclinic structure of $Ca_5Ge_3O_{11}$ and Nevsky, Ilyuskin *et al.* (1979) describe the orthorhombic form of a Ge-rich phase, $Ca_2Ge_7O_{16}$; neither of these two compounds is mentioned in the phase diagram of Shirvinskaya *et al.* (1966). Ca_2GeO_4 shows an olivine-type structure under ambient conditions (Eulenberger *et al.*, 1962), although the actual atomic arrangement is undetermined, and the structure of $CaGe_4O_9$ is unknown.

The title compound can be regarded as an additional new phase in the CaO–GeO_2 system, being close to $Ca_3Ge_2O_7$ in the phase diagram of Shirvinskaya *et al.* (1966). It is interesting to note that Barbier & Levy (1997) were not successful in reproducing a pure phase with nominal composition of $3CaO{\cdot}2GeO_2$. They noted that the actual composition of the '$Ca_3Ge_2O_7$' compound is $Ca_5Ge_3O_{11}$ (Barbier & Levy, 1997). The appearance of the additional $Ca_8Ge_5O_{18}$ phase is further evidence that the CaO–GeO_2 phase diagram is more complicated in detail than that given by Shirvinskaya *et al.* (1966) and probably needs additional work. It can be concluded that, instead of $Ca_3Ge_2O_7$ with 40 mol% GeO_2, two phases exist, having 37.5 ($Ca_5Ge_3O_{11}$) and 38.5 mol% ($Ca_8Ge_5O_{18}$) GeO_2, respectively.

Fig. 1 shows the asymmetric unit of the title compound as a displacement ellipsoid plot with the atomic numbering, while Fig. 2 is a polyhedral representation projected down the *a* axis. The structure contains isolated GeO_4 and Ge_3O_{10} groups and a band of Ca polyhedra, aligned parallel to the *c* axis (Fig. 2). Thus, the structure of the title compound appears to be unique, as these building units are not found in other Ca–Ge–O compounds. By sharing common edges and corners of Ge and Ca sites, a layer within the (100) plane is formed. These layers are stacked along the *a* axis in an *ABAB*... sequence. When viewing the Ge sites only, it is evident that the *B* layer is displaced along *b*/2 and inverted (Fig. 3). Here it also becomes evident that the Ca2, Ca3 and Ca5 sites reside in channels of the Ge framework, parallel to *c*.

Among the three Ge sites, the isolated Ge1 site is the most regular in terms of bond length distortions (Table 1). Each corner of the $Ge1O_4$ tetrahedron is attached to three neighbouring Ca sites. Thus, the O1–O2–O3 face of the Ge1 tetrahedron (forming the base) fits, by edge-sharing, into a triangular cavity, formed by the Ca1, Ca2 and Ca3 sites, which

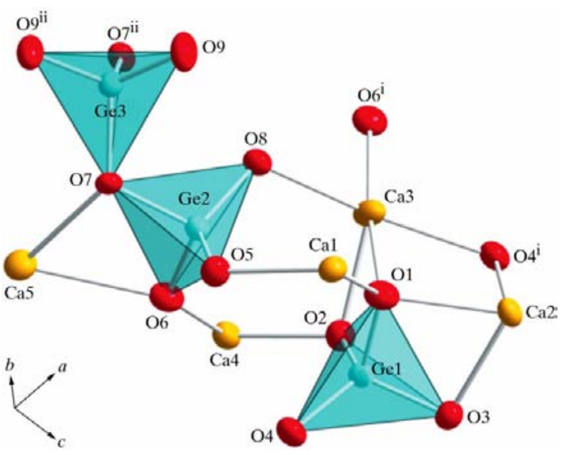

Figure 1
A view of the title compound, shown with 90% probability displacement ellipsoids. [Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, y, \frac{1}{2} - z$.]

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themselves share three common edges with each other (*cf.* Fig. 2). The congener of Ca1 is located at ($\frac{3}{2} - x$, $-\frac{1}{2} + y$, z) (symmetry code iii). Atom O4 is attached to three Ca sites [Ca1$^{\rm iv}$, Ca2$^{\rm v}$ and Ca3$^{\rm v}$; symmetry codes: (iv) $\frac{1}{2} - x$, $-\frac{1}{2} + y$, z; (v) $-1 + x$, y, z] of a next-lower (100) plane *via* corner-sharing. The tetrahedral O—Ge1—O angles involving the basal O atoms (O1, O2 and O3) are narrowed with respect to the ideal tetrahedral O—T—O angle and the angles involving O4 are opened up, with Ge1—O4 being the shortest of all four Ge1—O bonds. The distortion that gives rise to this prolate aspect of a tetrahedron is a trigonal C_{3v} elongation of the tetrahedron. As expected, the shared tetrahedral edges are noticeably shorter than the unshared ones (Table 1). Atoms Ge2, Ge3, and Ge2$^{\rm ii}$ [symmetry code: (ii) $1 - x$, y, $\frac{1}{2} - z$] form a trimer in which atom Ge2$^{\rm ii}$ is rotated by 180° about the *b* axis with respect to Ge2. This rotation is caused by the twofold axis residing upon the Ge3 site.

The Ge2 tetrahedron shares three of its corners with three neighbouring Ca sites; the fourth is common to the Ge3, Ca4$^{\rm vi}$ and Ca5 sites [symmetry code: (vi) $\frac{1}{2} - x$, $\frac{1}{2} + y$, z]. Similar to the Ge1 polyhedron, the O5–O6–O7 triangular face of the Ge2 tetrahedron fits into a triangular cavity formed by the Ca3, Ca4 and Ca5 sites (Fig. 2). Thus, three of the six tetrahedral edges are common to the tetrahedron and to Ca polyhedra. The fourth tetrahedral corner, atom O8, is shared between the Ge2, Ca3$^{\rm vii}$, Ca4$^{\rm vii}$ and Ca5$^{\rm i}$ sites [symmetry codes: (i) $1 + x$, y, z; (vii) $\frac{3}{2} - x$, $\frac{1}{2} + y$, z]. Similar to Ge1, the Ge2 tetrahedron exhibits a trigonal C_{3v} elongation towards this corner-shared O8 atom. The Ge2 site shows a larger polyhedral distortion, which is mainly due to the long Ge2—O7 bridging bond. Average shared und unshared edge lengths are similar for the Ge1 and Ge2 sites (Table 1). The bridging angle Ge3—O7—Ge2 is 115.47 (1)°, which is low compared with other compounds such as $Ca_5Ge_3O_{11}$ [Ge1—O5–Ge2 = 128.03 (15)°; Barbier & Levy 1997] or $CaGeO_3$ [Ge—O—Ge angles between 132.1 and 149.3°; Barbier & Levy, 1997]. In contrast with the Ge1 and Ge2 sites, no common edges with neighbouring polyhedra are present for the Ge3 site. Compared with the Ge1 and Ge2 sites, this results in a distinctly lower bond-angle distortion and elongation of the Ge3 site, while the bond-length distortion is still large due to the long Ge3—O7 bridging bond length (Table 1). Bond-valence sums are ideal for the Ge3 site, while the Ge1 and Ge2 sites appear to be under-bonded.

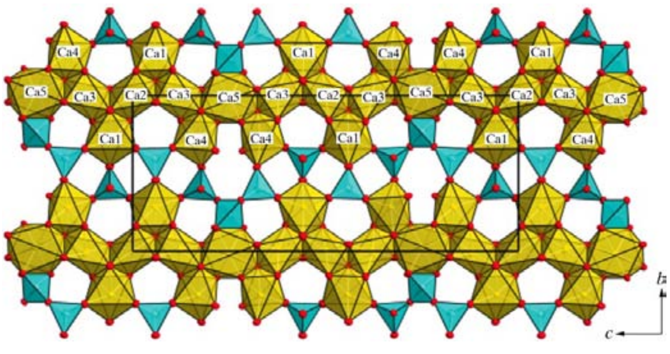

Figure 2
A polyhedral representation of the structure of the title compound, viewed along the crystallographic *a* axis. Only one (100) layer is shown.

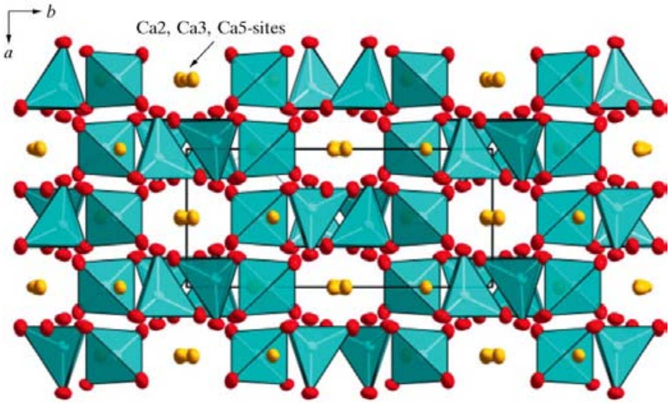

Figure 3
A polyhedral representation of the structure of the title compound, viewed along *c*. Polyhedra for the Ca sites have been omitted.

Two types of coordination polyhedra are found for the Ca sites: strongly distorted octahedral sites (Ca1–Ca4) and an eightfold coordinated site (Ca5). Connected *via* two common edges, the Ca2, Ca3 and Ca5 polyhedra form an infinite chain parallel to the crystallographic *c* axis. Thus, a Ca3–Ca2–Ca3$^{\rm viii}$ sequence [symmetry code: (viii) $2 - x$, $1 - y$, $1 - z$] is linked by the Ca5$^{\rm i}$ polyhedron (Fig. 2). Laterally attached to this chain by common edges are Ca1 and Ca4$^{\rm i}$ polyhedra. This arrangement gives rise to units of three edge-sharing Ca polyhedra, namely Ca1–Ca2–Ca3 and Ca3–Ca4–Ca5, forming a triangular cavity into which the bases of the Ge1 and Ge2 tetrahedra fit, thereby interconnecting different (100) layers along the crystallographic *a* axis. Ca—O bond lengths are similar for the sites Ca1–Ca4 but are distinctly longer at Ca5 (Table 1). Octahedral distortion parameters (Table 1) are high, particularly for the angular distortion. This shows that the Ca sites are far from an ideal octahedral coordination. Bond-valence sums for the Ca sites are close to 2.0, except for the Ca5 site.

Experimental

The title compound was discovered by chance during attempts to synthesize melilite-related $Ca_2CuGe_2O_7$ from a self-flux. A mixture of $CaCO_3$, CuO and GeO_2 in a $Ca_2CuGe_2O_7$ stoichiometry was carefully ground in an agate mortar and placed in a small platinum tube (length 30 mm, inner diameter 5 mm, one side welded tight and the other open). This assemblage was transferred to a high-temperature furnace, heated slowly to 1623 K at a rate of 1 K min^{-1}, held at this temperature for another 12 h to homogenize the melt, and cooled to 1323 K at a rate of 0.03 K min^{-1}. The synthesis batch mainly consisted of large colourless crystals of triclinic $CaGeO_3$ (Barbier & Levy 1997), some red–brown copper oxide and several small plate-like transparent crystals of the title compound, of a very pale-green colour. Qualitative energy-dispersive X-ray diffraction (REM–EDX; REM is raster electron microscopy) analysis of the pale-green crystals yielded Ca, Ge and O as the main elements, with a very minor Cu component also being present. A semi-quantitative EDX analysis yielded the structural formula $Ca_{7.96}Ge_{4.96}Cu_{0.07}O_{17.91}$;

the general formula can be given as $Ca_8Ge_5O_{18}$. In the phase diagram of Shirvinskaya *et al.* (1966), the title compound is very close to $Ca_3Ge_2O_7$ (the latter with 40 mol% GeO_2 and the former with 38.5 mol%).

Crystal data

$Ca_{7.96}Cu_{0.04}Ge_5O_{18}$
$M_r = 972.53$
Orthorhombic, *Pbcn*
$a = 5.2436$ (2) Å
$b = 11.6079$ (5) Å
$c = 28.9238$ (11) Å
$V = 1760.51$ (12) Å^3

$Z = 4$
$D_x = 3.669$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 10.90$ mm^{-1}
$T = 295$ (2) K
Plate, light green
0.12 × 0.11 × 0.08 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Rotation ω scans at four different φ positions
Absorption correction: numerical *via* equivalents using *X-SHAPE* (Stoe & Cie, 1996)
$T_{\min} = 0.29$, $T_{\max} = 0.42$

19710 measured reflections
2229 independent reflections
1930 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\max} = 28.8°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.059$
$S = 1.08$
2229 reflections
146 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 0.7889P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.93$ e Å^{-3}
$\Delta\rho_{\min} = -0.57$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00105 (9)

Structure solution using Patterson methods yielded the Ge and Ca positions. The O atoms were located from a residual electron-density analysis in a subsequent refinement cycle. After full anisotropic refinement on F^2, possible positions for the small Cu content were tested. While there was no evidence for occupation by Cu of the Ca1, Ca3, Ca4 and Ca5 positions, the Ca2 site refined to an occupancy of 4%. The amount of Cu, refined from the intensity data, agrees quite well with the amount found by semi-quantitative REM–EDX analysis. Five additional crystals of the same synthesis batch were tested, all giving the same unit-cell dimensions; on one of these additional crystals a full intensity data set was collected, yielding identical structural parameters within 1 s.u.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3041). Services for accessing these data are described at the back of the journal.

Table 1
Selected structural and polyhedral distortion parameters for the title compound.

	Ge1	Ge2	Ge3
Mean Ge—O (Å)	1.760	1.761	1.750
Mean O—O (Å)	2.863	2.857	2.857
BLD† (%)	0.46	2.14	2.39
Volume (Å^3)	2.749	2.729	2.739
TAV‡ (°)	52.63	79.71	11.68
TQE§	1.0120	1.0186	1.0034
S¶ (valence units)	3.87	3.89	4.00
	Ca1	Ca2	Ca3
Mean Ca—O (Å)	2.402	2.369	2.399
Mean O—O (Å)	3.376	3.334	3.359
BLD (%)	2.93	0.82	2.12
Volume (Å^3)	17.51	16.71	16.92
OAV†† (°)	131.50	144.73	205.00
OQE‡‡	1.0375	1.0404	1.0586
S (v.u.)	1.89	2.03	1.89
	Ca4	Ca5	
Mean Ca—O (Å)	2.371	2.554	
Mean O—O (Å)	3.338	3.113	
BLD (%)	3.73	4.20	
Volume (Å^3)	16.76	28.48	
OAV (°)	135.68		
OQE	1.0418		
S (v.u.)	2.08	1.73	

† Bond-length distortion (BLD) = $(100/n)\Sigma_{i=1}^{n}[\{(X{-}O)_i - (<X{-}O>)\}/(<X{-}O>)]$, where n = number of bonds, $(X{-}O)_i$ = central cation-to-oxygen length and $<X{-}O>$ = average cation-to-oxygen bond length (Renner & Lehmann, 1986). ‡ Tetrahedral angle variance (TAV) = $\Sigma_{i=1}^{n}(\Theta_i - 109.47)^2/5$ (Robinson *et al.*, 1971). § Tetrahedral quadratic elongation (TQE) = $\Sigma_{i=1}^{4}(l_i/l_t)^2/4$, where l_t = centre-to-vertex distance for a regular tetrahedron whose volume is equal to that of the undistorted tetrahedron with bond length l_i (Robinson *et al.*, 1971). ¶ Bond-valence sum (*S*) (Brese & O'Keeffe, 1991) †† Octahedral angle variance (OAV) = $\Sigma_{i=1}^{n}(\Theta_i - 90)^2/11$ (Robinson *et al.*, 1971). ‡‡ Octahedral quadratic elongation (OQE) = $\Sigma_{i=1}^{6}(l_i/l_o)^2/6$, where l_o = centre-to-vertex distance for a regular octahedron whose volume is equal to that of the undistorted octahedron with bond length l_i (Robinson *et al.*, 1971).

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