

Dicalcium heptagermanate  
 $\text{Ca}_2\text{Ge}_7\text{O}_{16}$  revisedGünther J. Redhammer,<sup>a\*</sup> Georg Roth<sup>b</sup> and Georg Amthauer<sup>a</sup><sup>a</sup>Department of Materials Engineering and Physics, Division of Mineralogy, University of Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria, and<sup>b</sup>Institute of Crystallography, RWTH Aachen University, Jägerstrasse 17/19, D-52056 Aachen, Germany

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The structure of dicalcium heptagermanate, previously described with an orthorhombic space group, has been redetermined in the tetragonal space group  $P\bar{4}b2$ . It contains three Ge positions (site symmetry 1, ..2 and 2.22, respectively), one Ca position (..2) and four O atoms, all on general  $8i$  positions (site symmetry 1). A sheet of four-membered rings of Ge tetrahedra (with Ge on the  $8i$  position) and isolated Ge tetrahedra (Ge on the  $4g$  position) alternate with a sheet of Ge octahedra (Ge on the  $2d$  position) and eightfold-coordinated Ca sites along the  $c$  direction in an  $ABABA \dots$  sequence. The three-dimensional framework of Ge sites displays a channel-like structure, evident in a projection on to the  $ab$  plane.

## Comment

In the system  $\text{CaO-GeO}_2$ , several phases are reported in the phase-equilibrium studies of Eulenberger *et al.* (1962) and Shirvinskaya *et al.* (1966), among them the Ge-rich phase  $\text{CaGe}_4\text{O}_9$ . Another Ge-rich phase is mentioned by Nevskii *et al.* (1979), namely  $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ . While the crystal structure of the first phase appears to be unknown at first glance, the latter was determined by Nevskii *et al.* (1979) to be orthorhombic [ $Pba2$ ,  $a = 11.340$  (2) Å,  $b = 11.340$  (2) Å and  $c = 4.6400$  (8) Å]. In order to investigate  $\text{CaGe}_4\text{O}_9$  in more detail and to determine its crystal structure, we attempted to synthesize this compound using ceramic sintering techniques between 1273 and 1473 K. However, we always identified very well crystallized  $\text{Ca}_2\text{Ge}_7\text{O}_{16}$  and small amounts of  $\text{GeO}_2$ . In addition, under hydrothermal conditions (923 K and 0.2 GPa), the stable phases are  $\text{Ca}_2\text{Ge}_7\text{O}_{16}$  and  $\text{GeO}_2$  (when starting with  $\text{CaGe}_4\text{O}_9$  composition). These findings led us to conclude that, in the phase diagram  $\text{CaO-GeO}_2$ , the compound  $\text{CaGe}_4\text{O}_9$  may not exist but has to be replaced by  $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ . This is supported by the fact that  $\text{Cd}_2\text{Ge}_7\text{O}_{16}$  was also described as 'Cd $\text{Ge}_4\text{O}_9$ ' in the literature (Wittmann 1966) until Plattner & Völlenklee (1977) evaluated its true chemistry by structure determination. This Cd compound is tetragonal, with  $a =$

11.31 Å and  $c = 4.63$  Å (space group  $P\bar{4}b2$ ). Germanates with  $AB_4X_9$ , such as  $\text{SrGe}_4\text{O}_9$  (Nishi, 1996),  $\text{BaGe}_4\text{O}_9$  (Shashkov *et al.*, 1984) and  $\text{PbGe}_4\text{O}_9$  (Shashkov *et al.*, 1981), display similar lattice parameters [e.g. 11.344 (2) and 4.750 (2) Å for  $\text{SrGe}_4\text{O}_9$ ] and structural topologies but have trigonal/rhombohedral symmetry (space group  $P321$ ).

Nevskii *et al.* (1979) report that  $\text{Ca}_2\text{Ge}_7\text{O}_{16}$  has Laue symmetry  $4/mmm$ , but the authors were unable to find a structural model in tetragonal symmetry. A reduction of symmetry led to orthorhombic space group  $Pba2$ . Nevskii *et al.* (1979) found a structural model with four Ge, one Ca and eight O-atom positions by a combination of Patterson methods and residual electron-density-map calculations and refined it down to  $R = 0.024$ . Motivated by the availability of small single crystals of the title compound from the hydrothermal experiment (923 K and 0.2 GPa) and large (up to 2 mm long) prismatic crystals from another synthesis experiment, where the title compound appeared by chance, the structure was reinvestigated and a revised model in tetragonal symmetry is given here.

The asymmetric unit of the title crystal structure contains one Ca, three Ge and four O-atom positions (Fig. 1). Four-membered rings of Ge1 tetrahedra, isolated Ge3 tetrahedra and Ge2 octahedra make up a three-dimensional framework that builds up two types of channels, which are evident in a projection parallel to the  $c$  axis (Fig. 2), *viz.* four-membered almost quadratic and eight-membered elliptical channels with diameters of  $\sim 3.54$  and  $3.99\text{--}6.25$  Å, respectively. The large cavities host the eightfold-coordinated Ca sites. In analogy to the topologically related  $AB_4X_9$  compounds mentioned above, the title compound may alternatively be described in terms of two different systems of sheets, which are stacked along the  $c$

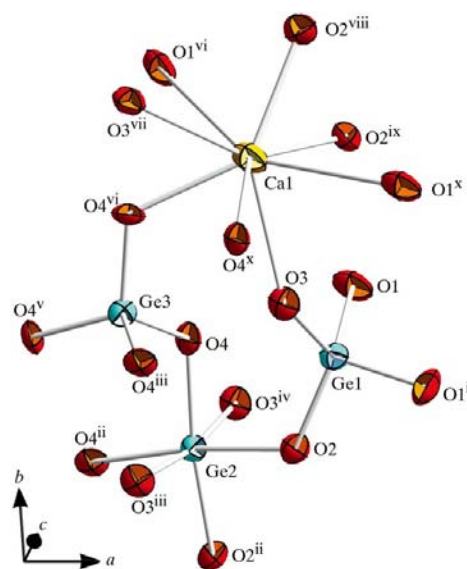


Figure 1

A view of the asymmetric unit and some symmetry-related atoms of the title compound, showing 95% probability displacement ellipsoids and the atomic numbering scheme. [Symmetry codes: (i)  $-y + 1, x, -z + 1$ ; (ii)  $-y + \frac{1}{2}, -x + \frac{1}{2}, -z$ ; (iii)  $-y + \frac{1}{2}, -x + \frac{1}{2}, -z + 1$ ; (iv)  $x, y, z - 1$ ; (v)  $-x, -y + 1, z$ ; (vi)  $y - \frac{1}{2}, x + \frac{1}{2}, -z + 1$ ; (vii)  $y - \frac{1}{2}, x + \frac{1}{2}, -z + 2$ ; (viii)  $-x + \frac{1}{2}, y + \frac{1}{2}, z + 1$ ; (ix)  $y, -x + 1, -z + 1$ ; (x)  $x, y, z + 1$ .]

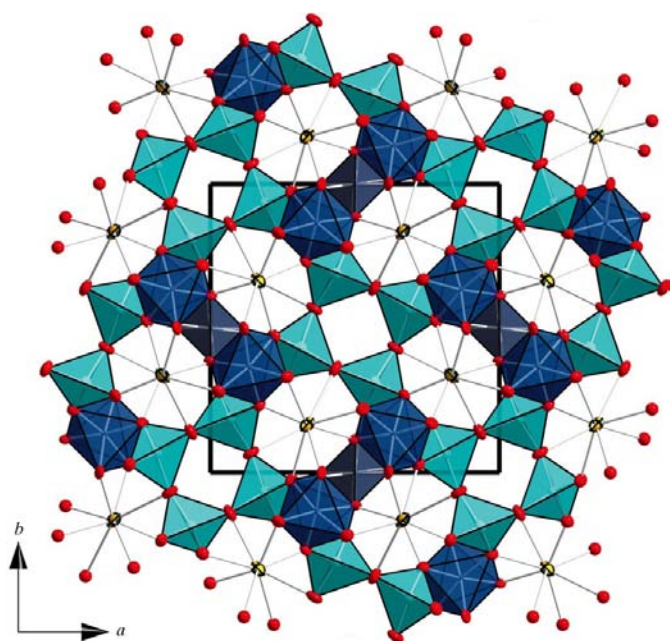
direction in an *ABABA* . . . sequence. The first of these sheets consists of the four-membered ring of Ge1 tetrahedra and the isolated Ge3 tetrahedra (Fig. 3), while the second sheet is composed of isolated Ge2 octahedra and the Ca sites. In contrast to the title compound, the trigonal structures exhibit three-membered rings of GeO<sub>4</sub> tetrahedra but no isolated tetrahedra, while the interconnection to a three-dimensional framework *via* the Ge octahedra is similar.

The Ge1 site, on general position *8i*, is coordinated by four O atoms as a distorted tetrahedron. Polyhedral distortion parameters are intermediately large (Table 2), which becomes evident when comparing especially tetrahedral angle variance (TAV) and tetrahedral quadratic elongation (TQE) parameters (Robinson *et al.*, 1971) with data previously found in other germanate compounds in the literature. The GeO<sub>4</sub> tetrahedron in Cu(Cu<sub>0.44</sub>Cr<sub>4.56</sub>)Ge<sub>2</sub>O<sub>12</sub> (Redhammer *et al.*, 2007) is an instance of a regular tetrahedron with distortion parameters TAV = 5.32° and TQE = 1.0013, while distinct distortion is found for tetrahedra in, for example, Ca<sub>7.96</sub>Cu<sub>0.04</sub>Ge<sub>5</sub>O<sub>18</sub>, with TAV = 79.71° and TQE = 1.0186° for the Ge2 site (Redhammer *et al.*, 2006). The angular distortion of the Ge1 tetrahedron in Ca<sub>2</sub>Ge<sub>7</sub>O<sub>16</sub> mainly results from the large O2–Ge1–O3 bond angle, interconnecting the Ge1 site *via* corner-sharing to two neighbouring Ge2 octahedra. *Via* atoms O1 and O1(–*y* + 1, *x*, –*z* + 1], the Ge1 tetrahedron is also connected to two neighbouring Ge1 tetrahedra, being part of the four-membered Ge<sub>1</sub>O<sub>12</sub> ring with the  $\bar{4}$  axis exactly in the centre of the ring. Within this ring, the Ge1–O1–Ge1(*y*, –*x* + 1, –*z* + 1) angle is 128.9 (2)°, a typical value for Ge–O–Ge angles. In the orthorhombic model of Nevskii *et al.* (1979), the Ge1 site is split up into two non-equivalent positions (Ge3 and Ge4) differing in average Ge–O bond lengths (1.757 and 1.768 Å) and showing bond-length distur-

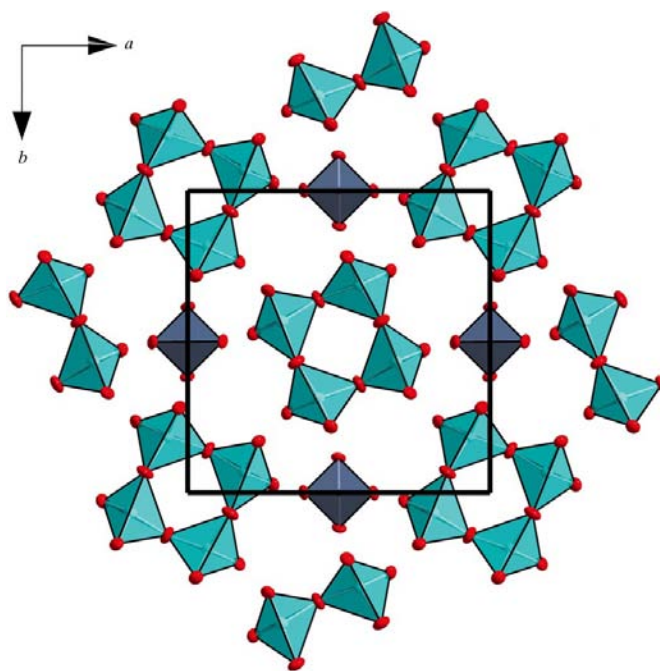
tions of 0.91 and 0.98%, respectively. By applying the orthorhombic model of Nevskii *et al.* (1979) to the present data, these differences in the two Ge sites could not be reproduced but rather the structural parameters are almost identical and differ by less than one standard deviation. Also the differences between the orthorhombic and the tetragonal model are less than one s.u. for the Ge sites of the four-membered ring. This also accounts for the Ge2 and Ge3 sites. In comparing with Cd<sub>2</sub>Ge<sub>7</sub>O<sub>14</sub> (Plattner & Völlenkle 1977), it is evident that the tetrahedron of the four-membered ring displays a smaller average Ge–O bond length but a somewhat larger polyhedral distortion in the Cd compound (Table 2).

The isolated Ge3 tetrahedron is located at the cell edges on special position *2d* (site symmetry 2.22) within the same sheet as the four-membered GeO<sub>4</sub> rings. While having four identical bond lengths as a result of symmetry restrictions (Table 1), thus BLD = 0.0, it exhibits distinct angular distortion and quadratic elongation, both being larger than for Ge1 (Table 2). All four corners (O4) are shared with neighbouring Ge2 octahedra (corner-sharing) and the Ca sites. In the Cd compound (Plattner & Völlenkle 1977), the isolated tetrahedron displays somewhat smaller bond and edge lengths and the angular distortion and elongation are lower (Table 2).

The octahedrally coordinated Ge2 site is on special position *4d* (site symmetry ..2). Four of its corners are shared with neighbouring Ge1 tetrahedra and the remaining two with neighbouring Ge3 tetrahedra. The average Ge2–O bond length in the title compound is somewhat larger than that found by Nevskii *et al.* (1979), but is smaller by ~0.01 Å than that in Cd<sub>2</sub>Ge<sub>7</sub>O<sub>16</sub> (Plattner & Völlenkle 1977). In comparing



**Figure 2**  
A view, along the *c* direction, of the structure of the title compound.



**Figure 3**  
A view, along the *c* direction, of the structure of the title compound, showing the sheet of four-membered rings of Ge1 tetrahedra and isolated Ge3 tetrahedra only.

$\text{Ca}_2\text{Ge}_7\text{O}_{16}$  and  $\text{Cd}_2\text{Ge}_7\text{O}_{16}$  with the  $AB_4\text{O}_9$  compounds it is found that average Ge—O bond lengths and polyhedral distortion parameters are similar. With increasing size of the eightfold-coordinated *A* cation [ $\text{Cd} = 1.07 \text{ \AA}$ ,  $\text{Ca} = 1.12 \text{ \AA}$ ,  $\text{Sr} = 1.25 \text{ \AA}$ ,  $\text{Pb} = 1.29 \text{ \AA}$  and  $\text{Ba} = 1.42 \text{ \AA}$ ; Shannon & Prewitt, 1969], an almost linear increase of  $\langle \text{Ge—O} \rangle$  bond lengths is observable, extending, for example, from 1.746 (2) and 1.762 (2)  $\text{ \AA}$  in the title compound to 1.756 (3) and 1.779 (3)  $\text{ \AA}$  for the tetrahedral sites in  $\text{BaGe}_4\text{O}_9$  (Shashkov *et al.*, 1984). The reverse is valid for the polyhedral distortion parameters, which distinctly decrease with increasing size of the *A* cations within the  $AB_4\text{O}_9$  series but also decrease from the title compound to  $\text{SrGe}_4\text{O}_9$  (Nishi, 1996), except for the Ge4 tetrahedron, which suffers extreme distortion in  $\text{SrGe}_4\text{O}_9$  (Nishi, 1996), with TAV = 159.9° and TQE = 1.0385. It might be concluded that the trigonal  $AB_4\text{O}_9$  structure type is not stable for cations smaller than Sr owing to this large distortion of the above-mentioned tetrahedral site, thus transforming to the similar tetragonal topology of the title compound.

The  $\text{Ca}^{2+}$  site is eight-coordinated, with six close and two more distant Ca—O bond lengths (Table 1). The two long bonds still contribute 0.08 valence units (v.u.) to the bond valence sum of  $\text{Ca}^{2+}$ , thus being regarded as bonding. While in  $\text{Ca}_2\text{Ge}_7\text{O}_{14}$ , the interstitial space hosting the *A* cation displays an elliptic shape and a non-uniform distribution of Ca—O bond lengths, it is of a more circular shape in  $\text{SrGe}_4\text{O}_9$ , displaying a more uniform distribution of Sr—O bonds between 2.600 (7) and 2.977 (8)  $\text{ \AA}$  (Nishi, 1996). It is assumed that the larger space requirement of  $\text{Sr}^{2+}$  (as compared with  $\text{Ca}^{2+}$ ) forces the formation of three-membered  $\text{GeO}_4$  rings, while in the title compound, four-membered rings are still possible.

## Experimental

The crystal used for crystal structure redetermination was obtained by chance during attempts to synthesize the clinopyroxene compound  $\text{CaFeGe}_2\text{O}_6$  under hydrothermal conditions from a highly saturated  $\text{CaCl}_2$  solution.  $\text{CaCl}_2$  was added to a homogenous mixture of  $\text{CaCO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{GeO}_2$  (with stoichiometry  $\text{CaFeGe}_2\text{O}_6$ ) in a 1:1 ratio. This starting material, together with 10 wt%  $\text{H}_2\text{O}$ , was placed in a gold capsule, which was welded closed and heated under hydrothermal conditions (923 K and 0.2 GPa, redox conditions of the Tuttle-type autoclave being close to nickel–nickel oxide solid-state buffer, 127 h run duration). The synthesis batch consisted of small idiomorphic crystals of Ge andradite  $\text{Ca}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$  (up to 30  $\mu\text{m}$  in size) and large colourless tetragonal prisms of the title compound (up to 2 mm in length and 200  $\mu\text{m}$  in diameter).  $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ , however, can also be obtained from stoichiometric mixtures of CaO and  $\text{GeO}_2$  using hydrothermal techniques (673–873 K and 0.2 GPa, 10 wt%  $\text{H}_2\text{O}$  added to the Au sample containers). The single crystals obtained here were distinctly smaller (maximum lengths of 80  $\mu\text{m}$ ).

### Crystal data

$\text{Ca}_2\text{Ge}_7\text{O}_{16}$	$Z = 2$
$M_r = 844.43$	Mo $K\alpha$ radiation
Tetragonal, $P4b2$	$\mu = 18.37 \text{ mm}^{-1}$
$a = 11.3391$ (6) $\text{ \AA}$	$T = 295$ (2) K
$c = 4.6371$ (2) $\text{ \AA}$	$0.15 \times 0.08 \times 0.07 \text{ mm}$
$V = 596.22$ (5) $\text{ \AA}^3$	

### Data collection

Bruker SMART APEX diffractometer	7055 measured reflections
Absorption correction: numerical via equivalents using <i>X-SHAPE</i> (Stoe & Cie, 1996)	764 independent reflections
$T_{\min} = 0.19$ , $T_{\max} = 0.28$	748 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.060$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	$\Delta\rho_{\text{max}} = 0.73 \text{ e \AA}^{-3}$
$wR(F^2) = 0.057$	$\Delta\rho_{\text{min}} = -0.81 \text{ e \AA}^{-3}$
$S = 1.15$	Absolute structure: (Flack, 1983),
764 reflections	296 Friedel pairs
60 parameters	Flack parameter: 0.03 (3)

**Table 1**

Selected geometric parameters ( $\text{ \AA}$ ,  $^\circ$ ).

Ge1—O3	1.747 (3)	Ge2—O4	1.913 (3)
Ge1—O2	1.758 (3)	Ge3—O4	1.746 (3)
Ge1—O1	1.759 (3)	Ca1—O4 <sup>vi</sup>	2.288 (3)
Ge1—O1 <sup>i</sup>	1.783 (3)	Ca1—O2 <sup>iii</sup>	2.297 (3)
Ge2—O3 <sup>iv</sup>	1.863 (3)	Ca1—O3	2.500 (3)
Ge2—O2	1.886 (3)	Ca1—O1 <sup>vi</sup>	2.924 (3)
O3—Ge1—O2	120.03 (16)	O2—Ge2—O2 <sup>ii</sup>	88.67 (19)
O3—Ge1—O1	105.40 (15)	O3 <sup>iv</sup> —Ge2—O4	83.83 (13)
O2—Ge1—O1	113.58 (14)	O3 <sup>iii</sup> —Ge2—O4	90.01 (13)
O3—Ge1—O1 <sup>i</sup>	104.00 (14)	O2—Ge2—O4	84.58 (13)
O2—Ge1—O1 <sup>i</sup>	102.64 (15)	O4—Ge2—O4 <sup>ii</sup>	102.24 (18)
O1—Ge1—O1 <sup>i</sup>	110.6 (2)	O4 <sup>vi</sup> —Ge3—O4 <sup>v</sup>	114.94 (19)
O3 <sup>iv</sup> —Ge2—O2	92.57 (14)	O4 <sup>vi</sup> —Ge3—O4	116.3 (2)
O3 <sup>iii</sup> —Ge2—O2	94.44 (14)	O4 <sup>v</sup> —Ge3—O4	97.77 (19)

Symmetry codes: (i)  $-y + 1, x, -z + 1$ ; (ii)  $-y + \frac{1}{2}, -x + \frac{1}{2}, -z$ ; (iii)  $-y + \frac{1}{2}, -x + \frac{1}{2}, -z + 1$ ; (iv)  $x, y, z - 1$ ; (v)  $-x, -y + 1, z$ ; (vi)  $y - \frac{1}{2}, x + \frac{1}{2}, -z + 1$ ; (viii)  $-x + \frac{1}{2}, y + \frac{1}{2}, z + 1$ .

The highest diffraction symmetry with reasonable  $R_{\text{int}}$  values is  $4/mmm$ ; thus, it was decided to facilitate structure solution using direct methods in tetragonal symmetry. Systematic extinction conditions allow space groups  $P4/mbm$ ,  $P4b2$  and  $P4bm$ . Only in the noncentrosymmetric space group  $P4b2$  was it possible to obtain a good solution with reliable agreement factors and realistic structural topology. For the other two cases it was not possible to obtain  $R$  values below 35%, and the coordination chemistry of the cations turned out to be highly unrealistic. It should be stressed that a structural model with tetragonal symmetry could be found and refined down to 5.7% in this study, while Nevskii *et al.* (1979) stated that they were unable to refine the structure with tetragonal symmetry as none of their models refined below 46%. We also tried to refine the structure of the title compound in orthorhombic symmetry. Here, space group  $Pba2$  of Nevskii *et al.* (1979) could be confirmed. The orthorhombic model works well too; the final reliability factors, however, are somewhat higher ( $wR2 = 6.7\%$ ) and thus it was decided that the tetragonal model was valid. In comparing the title compound with  $\text{Cd}_2\text{Ge}_7\text{O}_{16}$ , it became evident that there is a typing error in the atomic coordinates of Plattner & Völlenkle (1977) for O2, *viz.*  $z\text{O}2$  should read 0.228 instead of 0.288 given in their Table 2.

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

**Table 2**

Selected structural and polyhedral distortion parameters for the title compound compared with  $\text{Cd}_2\text{Ge}_7\text{O}_{16}$  (Plattner & Völlenklee, 1977).

	$\text{Ca}_2\text{Ge}_7\text{O}_{16}$	$\text{Cd}_2\text{Ge}_7\text{O}_{16}$
$\langle \text{Ge1-O} \rangle$ (Å)	1.762	1.741
$\langle \text{O-O} \rangle$ (Å)	2.871	2.836
BLD <sup>a</sup> (%)	0.59	0.92
Volume (Å <sup>3</sup> )	2.760	2.664
TAV <sup>b</sup> (°)	44.57	45.29
TQE <sup>c</sup>	1.0112	1.0112
S <sup>d</sup> (v.u.)	3.86	–
$\langle \text{Ge2-O} \rangle$ (Å)	1.746	1.740
$\langle \text{O-O} \rangle$ (Å)	2.847	2.839
BLD <sup>a</sup> (%)	0.00	0.00
Volume (Å <sup>3</sup> )	2.648	2.636
TAV <sup>b</sup> (°)	85.41	70.23
TQE <sup>c</sup>	1.0208	1.0173
S <sup>d</sup> (v.u.)	4.02	–
$\langle \text{Ge3-O} \rangle$ (Å)	1.888	1.896
$\langle \text{O-O} \rangle$ (Å)	2.670	2.682
BLD <sup>a</sup> (%)	0.92	1.72
Volume (Å <sup>3</sup> )	8.85	8.99
OAV <sup>e</sup> (°)	30.84	23.79
OQE <sup>f</sup>	1.0090	1.0074
S <sup>d</sup> (v.u.)	4.12	–
$\langle \text{Ca,Cd-O} \rangle$ (Å)	2.502	2.519
$\langle \text{O-O} \rangle$ (Å)	3.039	3.064
BLD <sup>a</sup> (%)	8.42	9.91
Volume (Å <sup>3</sup> )	26.29	26.74
S <sup>d</sup> (v.u.)	2.28	–

Notes: (a) bond length distortion (BLD) =  $(100/n) \sum_{i=1}^n [(X-O)_i - \langle (X-O) \rangle] / \langle (X-O) \rangle$ , where  $n$  is the number of bonds,  $(X-O)_i$  is the central cation-to-oxygen length and  $\langle (X-O) \rangle$  is the average cation–oxygen bond length (Renner & Lehmann, 1986); (b) tetrahedral angle variance (TAV) =  $\sum_{i=1}^n (\Theta_i - 109.47)^2 / 5$  (Robinson *et al.*, 1971), where  $\Theta_i$  is the individual O–T–O angle (where T is the tetrahedral cation); (c) tetrahedral quadratic elongation (TQE) =  $\sum_{i=1}^4 (l_i / l_o)^2 / 4$ , where  $l_i$  is the centre-to-vertex distance for a regular tetrahedron whose volume is equal to that of the undistorted tetrahedron with bond length  $l_o$  (Robinson *et al.*, 1971); (d) bond valence sum (S; Brese & O’Keeffe, 1991); (e) octahedral angle variance (OAV) =  $\sum_{i=1}^n (\Theta_i - 90)^2 / 11$  (Robinson *et al.*, 1971); (f) octahedral quadratic elongation (OQE) =  $\sum_{i=1}^6 (l_i / l_o)^2 / 6$ , with  $l_o$  = centre to vertex distance for a regular octahedron whose volume is equal to that of the undistorted octahedron with bond length  $l_o$  (Robinson *et al.*, 1971).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3088). Services for accessing these data are described at the back of the journal.

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