

Commensurate monoclinic form of $\text{Ca}_2\text{Zn}_{0.97}\text{Co}_{0.03}\text{Ge}_2\text{O}_7$

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Cobalt-doped dicalcium zinc germanate, synthesized by slow cooling from the melt, is monoclinic and has a layered structure, which is different from the modulated melilite-type structure of $\text{Ca}_2\text{ZnGe}_2\text{O}_7$. The monoclinic form has two different Ca, one Zn and two Ge sites, and seven independent O-atom positions; all are in general position 4e of the space group $P2_1/n$. The topology of the structure is described and compared with that of $\text{Ca}_2\text{ZnGe}_{1.25}\text{Si}_{0.75}\text{O}_7$.

Comment

Minerals/compounds with the general formula $A_2BC_2X_7$ (A is a large cation such as Ba, Sr and Ca; B is a small four-coordinated metal cation such as Mg, Zn, Co and Ni; $C = \text{Si}$ and Ge; $X = \text{O}$) most frequently belong to the group of melilite-type structures. They show tetragonal symmetry and several of them are known to be incommensurately modulated, e.g. $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and $\text{Ca}_2\text{CoSi}_2\text{O}_7$ (Seifert *et al.*, 1987; Hemingway *et al.*, 1986; Riestler & Böhm, 1997). It has been suggested that this temperature-dependent modulation may be due to the

structural misfit between the large A cations and the framework of five-membered rings of B and C tetrahedra (Van Heureck *et al.*, 1992; Hemingway *et al.*, 1986; Seifert *et al.*, 1987). For $\text{Ca}_2\text{ZnGe}_2\text{O}_6$, Armbruster *et al.* (1990) report two polymorphs. High- $\text{Ca}_2\text{ZnGe}_2\text{O}_7$ possesses an incommensurately modulated structure at room temperature; the average structure can be described in the space group $P\bar{4}2_1m$, which is the typical symmetry of melilite-type compounds. Van Heureck *et al.* (1992) confirmed the modulated structure of high- $\text{Ca}_2\text{ZnGe}_2\text{O}_7$ using high-resolution transmission electron microscopy. Low- $\text{Ca}_2\text{ZnGe}_2\text{O}_7$, grown at much lower temperature from an Na_2WO_4 flux by Armbruster *et al.* (1990), also displays a modulated fine structure; however, the average structure was described in the monoclinic system (space group $P2_1$). The latter polymorph represents a stacking variant of melilite-like layers with an $ABA'ABA'$ stacking sequence (Armbruster *et al.*, 1990). These authors also report the synthesis of a new tetrahedral sheet structure with composition $\text{Ca}_2\text{ZnGe}_{1.25}\text{Si}_{0.75}\text{O}_7$ at a low temperature of 723 K using hydrothermal techniques. This structure is monoclinic (space group $P2_1/n$) and well ordered. In the present paper, the structure refinement of weakly Co-doped unmodulated $\text{Ca}_2\text{ZnGe}_2\text{O}_6$ is presented and compared with that of $\text{Ca}_2\text{ZnGe}_{1.25}\text{Si}_{0.75}\text{O}_7$ described previously by Armbruster *et al.* (1990).

The structure of the title compound consists of layers of corner-sharing tetrahedra running parallel to (101). The layers consist of Ge_2O_7 groups linked by ZnO_4 tetrahedra and are separated by Ca atoms. Fig. 1 shows a displacement ellipsoid plot of the title compound, including atomic nomenclature, while Figs. 2 and 3 display polyhedral representations in different orientations. While in the melilite-type structure only five-membered rings occur, the tetrahedral layer in the title compound consists of four-, five- and strongly deformed six-membered rings (shaded areas in Fig. 2). As described by Armbruster *et al.* (1990), the layers are stacked in an $ABAB$ sequence, where the A and B layers are symmetrically

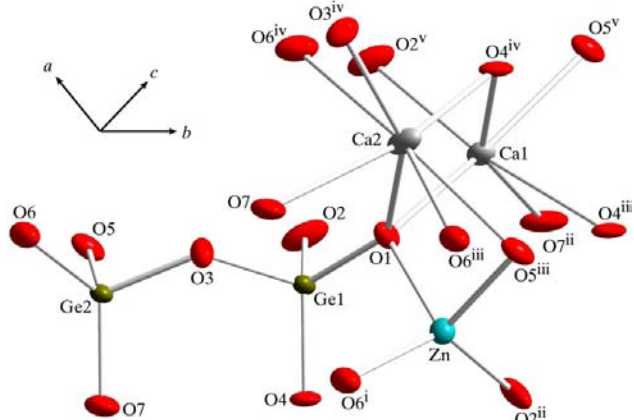


Figure 1

A view of (I) (90% probability displacement ellipsoids). [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, y + 1, z$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + 1, -y + 1, -z + 2$.]

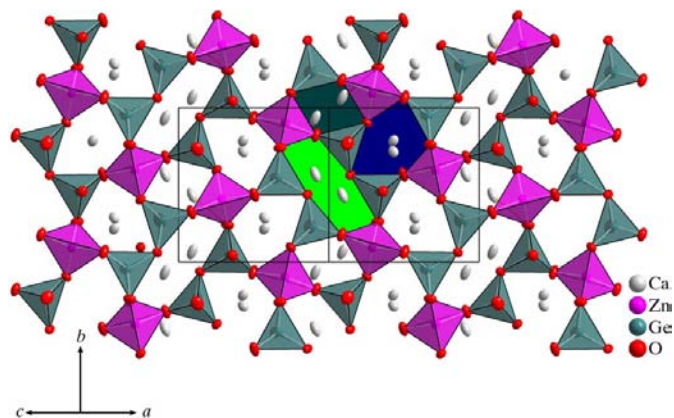


Figure 2

A polyhedral representation of a tetrahedral layer of (I), viewed parallel to [101]. Ca atoms above and below the tetrahedral layer are shown, and the four-, five- and six-membered rings of tetrahedra are outlined by shading.

equivalent but shifted relative to each other along $[101]/2$. The average Ge–O bond lengths for the Ge1 and Ge2 tetrahedra are identical; however, the polyhedral volume is smaller and the bond length distortion (BLD; Renner & Lehmann, 1986), tetrahedral angle variance and mean quadratic elongation (TAV and TQE; Robinson *et al.*, 1971) are larger for the Ge2 site, revealing this site to be more distorted (Table 1). The larger angular distortion of the Ge2 site is mainly due to a large O7–Ge2–O5 bonding angle of $122.3(1)^\circ$, opposite the O7–O5 tetrahedral edge length of $3.036(2) \text{ \AA}$, which is the longest among all the tetrahedral edges. It can be concluded that within the monoclinic non-modulated structure of $\text{Ca}_2\text{ZnGe}_2\text{O}_7$ (this study), the Ge tetrahedra are much more regular than those in the tetragonal and monoclinic modulated forms described by Armbruster *et al.* (1990). Owing to the exclusive occupation of Ge1 and Ge2 sites by germanium, individual and average bond lengths are distinctly larger (Table 1) in the title compound than in $\text{Ca}_2\text{ZnGe}_{1.25}\text{Si}_{0.75}\text{O}_7$ of Armbruster *et al.* (1990). For both sites, the replacement of Ge by Si causes a reduction of tetrahedral distortion, which is more evident for the Ge2 site (Table 1). As the Ge2 site is smaller even in $\text{Ca}_2\text{ZnGe}_2\text{O}_7$, it may be argued that this site is more accessible for Si incorporation, as has been observed by Armbruster *et al.* (1990). The Ge1–O3–Ge2 angle is remarkably small [$119.7(1)^\circ$]; Si substitution causes an increase of this angle to 122° (Armbruster *et al.*, 1990), while in $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ (hardystonite), the Si–O1–Si angle is $141.47(8)^\circ$ (Louisnathan, 1969). Bond valence sums, S (Bresle & O’Keeffe, 1991), for the two Ge sites in the title compound are close to the ideal values of 4.0 valence units (v.u.); the valence sums for the coordinating O atoms are between 1.9 and 2.10 v.u., except for O7 with $S = 1.58$ v.u. and O4 with $S = 1.84$ v.u. The former is bonded to atoms Ge2, Ca1 and Ca2, while the latter O atom has bonds to Ge1, two Ca1 and one Ca2 sites. The highest bond valence sum is found for atom O3, which is bonded to atoms Ge1, Ge2 and Ca2 ($S = 2.10$ v.u.).

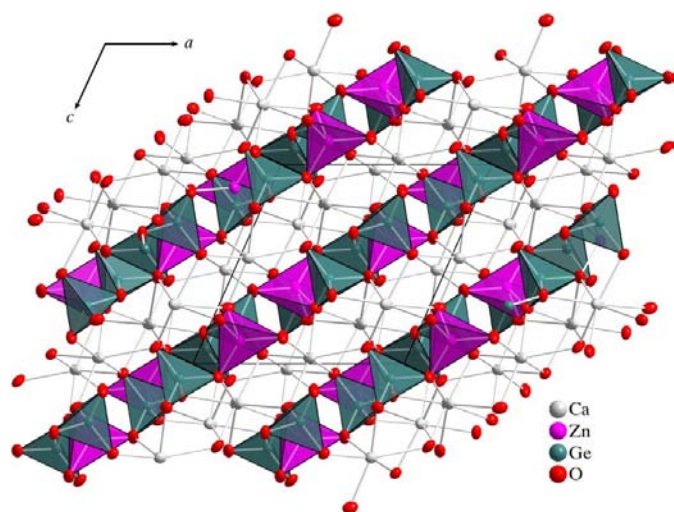


Figure 3

A polyhedral representation of (I), viewed along $[010]$, displaying the layered character of the structure.

Individual and average bond and edge lengths of the ZnO_4 tetrahedra are of comparable size in the title compound and in $\text{Ca}_2\text{ZnGe}_{1.25}\text{Si}_{0.75}\text{O}_7$, while the TAV and TQE are lower for the Ge end member. Generally, this site appears to be distinctly distorted (Table 1). The valence sum of the Zn atom is 2.09 v.u., which is close to the ideal value.

The Ca atoms reside within two different types of channels running along $[101]$. The Ca1 site is hosted in a channel arising from the stacking of the five-membered rings of tetrahedra that are rotated relative to each other. Here, Ca1 is in a distorted sixfold O-atom coordination. The volume, angular variance and quadratic elongation of this octahedron are large (Table 1). Individual and average Ca1–O bond lengths and distortion parameters are almost identical in the pure Ge and the Si-substituted compound (Table 1), suggesting that tetrahedral substitution has a minor influence on the bonding characteristics of the Ca1 site. The Ca2 site is located in a channel that is formed by the alternate stacking of four- and six-membered rings, and it is eightfold coordinated. The average Ca2–O bond is larger than the average Ca1–O bond but is of similar size to the equivalent bond in the Armbruster *et al.* (1990) compound (Table 1). Both Ca sites are distinctly under-bonded, with bond valence sums of 1.82 and 1.74 v.u.

Experimental

The title compound was obtained by chance during the synthesis of germanate clinopyroxenes in the system $\text{CaZnGe}_2\text{O}_6$ – $\text{CaNiGe}_2\text{O}_6$. Pressed tablets of a homogeneous finely ground mixture of CaCO_3 , NiO, ZnO and GeO_2 in the stoichiometry $\text{CaZn}_{0.5}\text{Ni}_{0.5}\text{Ge}_2\text{O}_6$ were placed in an open platinum crucible, fired to 1598 K at a rate of 100 K h^{-1} , held at this temperature for 12 h to ensure complete melting and cooled slowly to 1373 K at a rate of 6 K h^{-1} afterwards. The experiment yielded large yellow clinopyroxene crystals of up to 2 mm in size. In addition, a small amount (<1 wt%) of emerald-green cubic spinel NiGe_2O_4 and some pale-pink crystals of the title compound were formed. The colour of the title compound results from traces of cobalt. It should be noted that at the same time an experiment to grow the $\text{CaCoGe}_2\text{O}_6$ clinopyroxene compound was performed in the same high-temperature furnace. The presence of cobalt in the title compound was validated by electron microprobe chemical analysis, yielding the following chemical composition (in wt%): 27.86 CaO, 19.71 ZnO, 0.56 CoO, 51.71 GeO_2 . This corresponds to a structural formula of $\text{Ca}_{2.01(2)}\text{Zn}_{0.98(2)}\text{Co}_{0.03(1)}\text{Ge}_{2.00(1)}\text{O}_7$. No nickel was found in this compound.

Crystal data

$\text{Ca}_2\text{Zn}_{0.97}\text{Co}_{0.03}\text{Ge}_2\text{O}_7$
 $M_r = 402.53$
 Monoclinic, $P2_1/n$
 $a = 9.1608(8) \text{ \AA}$
 $b = 7.9863(7) \text{ \AA}$
 $c = 9.4590(8) \text{ \AA}$
 $\beta = 113.9084(12)^\circ$
 $V = 632.65(9) \text{ \AA}^3$

$Z = 4$
 $D_x = 4.227 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 14.78 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Cuboid, pink
 $0.15 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: numerical
 via equivalents using *X-SHAPE*
 (Stoe & Cie, 1996)
 $T_{\min} = 0.13$, $T_{\max} = 0.24$

5971 measured reflections
 1517 independent reflections
 1386 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\text{max}} = 28.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.053$
 $S = 1.07$
 1517 reflections
 112 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 0.4636P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.69 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.82 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0198 (8)

Table 1

Selected geometric parameters for $\text{Ca}_2\text{ZnGe}_2\text{O}_7$ compared with those of $\text{Ca}_2\text{ZnGe}_{1.25}\text{Si}_{0.75}\text{O}_7$, calculated from atomic coordinates given by Armbruster *et al.* (1990).

	$\text{Ca}_2\text{ZnGe}_2\text{O}_7$	$\text{Ca}_2\text{ZnGe}_{1.25}\text{Si}_{0.75}\text{O}_7$
Ge1 site		
$\langle\text{Ge1}-\text{O}\rangle$ (Å)	1.753 (2)	1.721 (2)
$\langle\text{O}-\text{O}\rangle$ (Å)	2.858 (2)	2.806 (2)
BLD ^a (%)	1.07	1.06
Vol. (Å ³)	2.74	2.60
TAV ^b (°)	21.15	20.79
TQE ^c	1.0051	1.0050
S^d (v.u.)	3.95	4.14
Ge2 site		
$\langle\text{Ge2}-\text{O}\rangle$ (Å)	1.752 (2)	1.694 (2)
$\langle\text{O}-\text{O}\rangle$ (Å)	2.851 (2)	2.757 (2)
BLD ^a (%)	1.11	1.30
Vol. (Å ³)	2.70	2.45
TAV ^b (°)	62.86	54.14
TQE ^c	1.0145	1.0123
S^d (v.u.)	3.96	4.07
Zn site		
$\langle\text{Zn}-\text{O}\rangle$ (Å)	1.947 (2)	1.944 (2)
$\langle\text{O}-\text{O}\rangle$ (Å)	3.149 (2)	3.143 (2)
BLD ^a (%)	1.98	1.85
Vol. (Å ³)	3.63	3.61
TAV ^b (°)	112.76	125.63
TQE ^c	1.0280	1.0309
S^d (v.u.)	2.09	2.25
Ca1 site		
$\langle\text{Ca1}-\text{O}\rangle$ (Å)	2.417 (2)	2.419 (2)
$\langle\text{O}-\text{O}\rangle$ (Å)	3.379 (2)	3.380 (2)
Vol. (Å ³)	17.43	17.42
OAV ^e	172.86	176.98
OQE ^f	1.0546	1.0560
S^d (v.u.)	1.82	1.74
Ca2 site		
$\langle\text{Ca2}-\text{O}\rangle$ (Å)	2.577 (2)	2.569 (2)
$\langle\text{O}-\text{O}\rangle$ (Å)	3.201 (2)	3.196 (2)
Vol. (Å ³)	29.22	28.93
S^d (v.u.)	1.74	1.72

Notes (a) bond length distortion, $\text{BLD} = (100/n) \sum_{i=1}^n \{ |(X-\text{O})_i - \langle X-\text{O} \rangle| / \langle X-\text{O} \rangle \}$, with n = number of bonds, $(X-\text{O})_i$ = central-cation-to-oxygen length and $\langle X-\text{O} \rangle$ = average cation-oxygen bond length (Renner & Lehmann, 1986); (b) tetrahedral angle variance, $\text{TAV} = \sum_{i=1}^n (\Theta_i - 109.47) / 5$ (Robinson *et al.*, 1971); (c) tetrahedral quadratic elongation, $\text{TQE} = \sum_{i=1}^4 (l_i/l_o)^2 / 4$ (Robinson *et al.*, 1971); (d) bond valence sum, S (Brese & O'Keeffe, 1991); (e) octahedral angle variance, $\text{OAV} = \sum_{i=1}^n (\Theta_i - 90) / 11$ (Robinson *et al.*, 1971); (f) octahedral quadratic elongation, $\text{OQE} = \sum_{i=1}^6 (l_i/l_o)^2 / 6$, 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_i (Robinson *et al.*, 1971).

Experimental image-plate data could be indexed on the basis of a monoclinic unit cell; no superstructure or satellite reflections were found in reconstructed precession images. Attempts to index the data on the basis of a tetragonal or monoclinic cell similar to those used by Armbruster *et al.* (1990) failed. Analysis of systematic extinction rules and E statistics confirmed the space group $P2_1/n$. After full anisotropic refinement of all parameters on F^2 , an occupation of Ca1, Ca2 and Zn sites with Co was tested. Only for the Zn site was a weak significant positive occupation found, and thus Co was assigned to the tetragonally coordinated Zn site. We are aware that the scattering power is very similar for Zn and Co. However, as the amount of Co indicated from structure refinement is close to that determined from electron microprobe analysis, the procedure used seems to be justified. A second data set, collected on a Bruker SMART APEX diffractometer at the University of Salzburg, yielded identical results, including the same amount of Co on the Zn site. As the data set from the image plate extends to larger diffraction angles, results from the Stoe IPDS measurement are presented here.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3005). Services for accessing these data are described at the back of the journal.

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