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The structure of diyttrium digermanate, $Y_2Ge_2O_7$, has been determined in the tetragonal space group $P4_32_12$. It contains one Y, one Ge (both site symmetry 1 on general position 8b) and four O atoms [one on special position 4a (site symmetry ..2) and the remaining three on general positions 8b]. The basic units of the structure are isolated Ge_2O_7 groups, sharing one common O atom and displaying a Ge—O—Ge angle of $134.9(3)^\circ$, and infinite helical chains of pentagonal YO_7 dipyramids, parallel to the 4_3 screw axis. The crystal investigated here represents the left-handed form of the tetragonal $R_2Ge_2O_7$ compounds ($R = Eu^{3+}$, Tb^{3+} , Er^{3+} , Tm^{3+} and Lu^{3+}).

Comment

The pyrogermanates of the rare-earth elements have attracted some interest owing to their properties, in particular their optical activity (Stadnicka *et al.*, 1990; Das *et al.*, 1999). The first high-quality single crystals of the $R_2Ge_2O_7$ series with $R = Tb^{3+}$ – Lu^{3+} were grown by Wanklyn (1973) using flux growth techniques. Smolin (1970) reported that powder samples of $R_2Ge_2O_7$ with $R = Yb^{3+}$, Er^{3+} , Ho^{3+} , Y^{3+} , Dy^{3+} and Tb^{3+} are tetragonal. Bondar (1979) published refractive indices for the La^{3+} , Nd^{3+} , Gd^{3+} , Y^{3+} (assumed to be triclinic) and Er^{3+} (tetragonal) pyrogermanates. Subsequently, complete structure determinations have been published for $Eu_2Ge_2O_7$ (Chiragov *et al.*, 1983), $Tb_2Ge_2O_6$ (Geller & Gaines, 1987), $Er_2Ge_2O_7$ (Smolin, 1970), $Tm_2Ge_2O_7$ (Stadnicka *et al.*, 1990) and $Lu_2Ge_2O_7$ (Palinka *et al.*, 1995). All of these compounds are tetragonal, space group $P4_12_12$, confirming the observation of Smolin (1970) that the lanthanide pyrogermanate series Eu and Tb–Lu appears to be isostructural. $La_2Ge_2O_7$ (Vetter & Queyroux, 1988), $Nd_2Ge_2O_7$ (Vetter *et al.*, 1982) and $Gd_2Ge_2O_7$ (Smolin *et al.*, 1971) are triclinic.

In the present contribution, the structure of the pyrogermanate $Y_2Ge_2O_7$ is found to be tetragonal, space group $P4_32_12$. This is in disagreement with the previous assumption of a triclinic structure for the title compound given by Bondar

(1979) and confirms the findings of tetragonal symmetry by Smolin (1970). The absolute configuration of $Y_2Ge_2O_7$, however, is different from that of the other lanthanide pyrogermanates $R_2Ge_2O_7$, which are reported to crystallize in the space group $P4_12_12$. Refinement of the structure of $Tm_2Ge_2O_7$ in $P4_32_12$ ($\bar{x}\bar{y}\bar{z}$) by Stadnicka *et al.* (1990) yielded final agreement factors above 0.3; thus, Stadnicka *et al.* (1990) concluded that their crystal is the $P4_12_12$ (xyz) enantiomorph. The opposite is true for $Y_2Ge_2O_7$ (see description of refinement below).

The lattice parameters of the pyrogermanate series $R_2Ge_2O_7$ ($R = Eu$ and Tb – Lu) define an almost linear increase with the ionic radius of the R cation, as given by Shannon & Prewitt (1969), for both the a and the c parameter. The smallest values are found for $Lu_2Ge_2O_7$ [$a = 6.702(5)$ Å and $c = 12.175(11)$ Å (Palinka *et al.*, 1995)] and the largest lattice parameters are found in $Eu_2Ge_2O_7$ [$a = 6.909$ Å and $c = 12.558$ Å (Chiragov *et al.*, 1983)]. The data for the title compound perfectly fit into those of the $R_2Ge_2O_7$ series.

The asymmetric unit of $Y_2Ge_2O_7$ contains one Y-, one Ge- and four O-atom positions (Fig. 1). The Ge^{4+} ion is coordi-

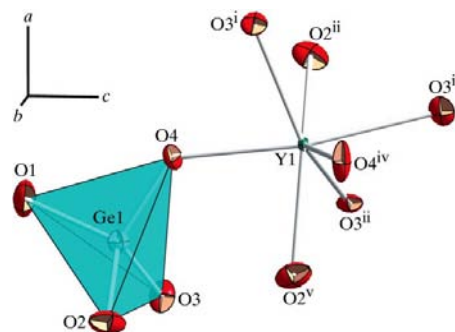


Figure 1

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) $y, x + 1, -z + 1$; (ii) $y - \frac{1}{2}, -x + \frac{1}{2}, z + \frac{1}{4}$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{5}{4}$; (iv) $y - \frac{1}{2}, -x + \frac{3}{2}, z + \frac{1}{4}$; (v) $y - 1, x + 1, -z + 1$.]

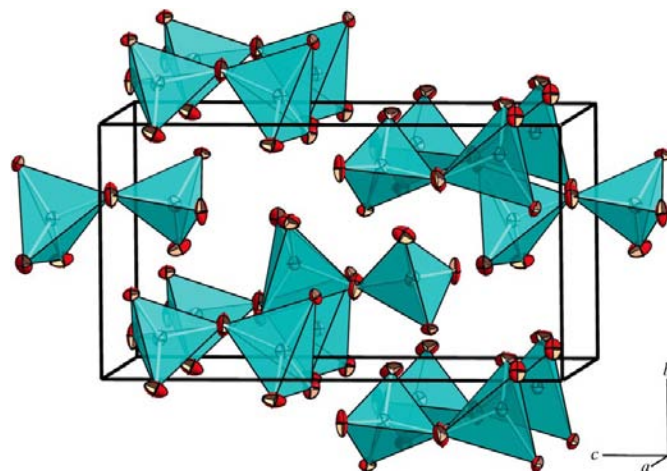


Figure 2

A polyhedral representation of the structure of $Y_2Ge_2O_7$ with only the ditetrahedral Ge_2O_7 units shown.

nated by a tetrahedron of four non-equivalent O atoms. Two GeO_4 tetrahedra are connected to each other *via* the corner of atom O1, forming isolated $[\text{Ge}_2\text{O}_7]^{6-}$ units (Fig. 2). The Ge1—O1—Ge1 bridging angle is $134.9(3)^\circ$. This is one major difference from the yttrium pyrosilicate $\text{Y}_2\text{Si}_2\text{O}_7$, which has a straightened $(\text{Si}_2\text{O}_7)^{6-}$ configuration (Redhammer & Roth, 2003). The same pyro-group configuration is also found in $\text{Er}_2\text{Si}_2\text{O}_7$, $\text{Ho}_2\text{Si}_2\text{O}_7$, $\text{Tm}_2\text{Si}_2\text{O}_7$ and $\text{Yb}_2\text{Si}_2\text{O}_7$, which all show Si—O—Si angles of 180° and are isostructural with thortveitite, $\text{Sc}_2\text{Si}_2\text{O}_7$ (Smolin, 1970). Within the lanthanide pyrogermanate series, the Ge—O—Ge angle ranges between $130.0(1)$ and $136.0(4)^\circ$ (Table 2); however, no systematic variation is found from literature data. Individual Ge—O bond lengths in $\text{Y}_2\text{Ge}_2\text{O}_7$ range between $1.733(3)$ and $1.780(3)$ Å. The two shorter bonds, *viz.* Ge1—O2 and Ge1—O4, are to O atoms bonded to two additional Y atoms, while the longest (Ge1—O3) is to an O atom bonded to three Y atoms along with the Ge atom. This fourfold-coordinated O atom obviously contributes less bond strength to the Ge atom; the corresponding Ge—O bond is therefore longer. Smolin (1970) made a similar observation for $\text{Er}_2\text{Ge}_2\text{O}_7$, where the O atom coordinated by three rare-earth ions also formed the longest bond to its nearest Ge neighbour. Owing to the large variation of the individual Ge—O bond lengths, the GeO_4 tetrahedron in $\text{Y}_2\text{Ge}_2\text{O}_7$ shows large polyhedral distortion parameters (Table 2). Average Ge—O bond lengths in the pyrogermanate series $R_2\text{Ge}_2\text{O}_7$ are similar, with a tendency towards an increase of $\langle\text{Ge—O}\rangle$ with increasing radius of the *R* cation. The tetrahedral angle variance (TAV) and the tetrahedral quadratic elongation (TQE) in the title compound are generally high and are among the largest found for germanium compounds. Regular GeO_4 tetrahedra, as realized in the compound $\text{Cu}(\text{Cu}_{0.44}\text{Cr}_{4.56})\text{Ge}_2\text{O}_{12}$, have TAV and TQE values of 5.32° and 1.0013 (Redhammer *et al.*, 2007a), while intermediate distortions with TAV values of $\sim 80^\circ$ are found, for example, in norbergite-type $\text{Ca}_3\text{Ge}_4\text{Cl}_2$ (Redhammer *et al.*, 2007b) and in $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ (Redhammer *et al.*, 2007c). TAV and TQE values decrease distinctly with increasing radius of *R*

in the $R_2\text{Ge}_2\text{O}_7$ series, remaining constant above a radius of ~ 1.0 Å (Er^{3+}). The values for the title compound, again, perfectly fit the data for the lanthanide series. The GeO_4 tetrahedron shares one edge with a neighbouring Y polyhedron; this O2—O3 edge is the shortest of all tetrahedral edges [$2.600(2)$ Å], and the angle opposite this edge is the smallest O—Ge—O bonding angle [$95.3(1)^\circ$]. All other edges are unshared and are thus distinctly longer. The bond-valence sum (Brese & O'Keeffe, 1991) of Ge^{4+} is close to the ideal value [$S = 3.94$ valence units (v.u.)], atom O1, bonded to the two Ge atoms of the Ge_2O_7 unit, is slightly under-bonded ($S = 1.89$ v.u.), atoms O2 and O3, bonded to two and three Y atoms, respectively, reveal ideal bond-valence sums ($S = 2.00$ v.u.), while atom O4 is over-bonded ($S = 2.07$ v.u.).

Y^{3+} is sevenfold coordinated by O atoms; the coordination polyhedron can be described as a distorted pentagonal bipyramid with the pyramidal axis almost parallel to the *c* direction. Within the tetragonal $R_2\text{Ge}_2\text{O}_7$ series the average *R*—O bond lengths are positively and linearly correlated with the ionic radius of the *R* cation. The average Y—O bond length of the title compound goes along with this trend (Tables 1 and 2). The YO_7 polyhedron shares the O3($y, 1+x, 1-z$)—O4 and O3($-\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{4}+z$)—O4($-\frac{1}{2}+y, \frac{3}{2}-x, \frac{1}{4}+z$) edges, both $2.818(4)$ Å in length, with two neighbouring YO_7 polyhedra to form helical left-handed chains along the 4_3 axis (Fig. 3). Three additional edges of the YO_7 polyhedron are shared with neighbouring YO_7 polyhedra belonging to two different helical chains; one O—O edge is common to the YO_7 polyhedron and the GeO_4 tetrahedron, and the remaining nine edges are unshared. The difference between the average of the shared edges [$3.329(4)$ Å] and that of the unshared edges [$2.797(4)$ Å] is large. This indicates distinct distortion of the YO_7 polyhedron, which is also expressed by the large bond-length distortion parameter (Table 1). The bond-valence sum for Y^{3+} is almost ideal ($S = 3.11$ v.u.).

Experimental

As part of the investigation of the crystal chemistry of (Na,Li)- Ge_2O_6 1:3 germanate clinopyroxene compounds, the title compound was obtained by chance during attempts to synthesize LiYGe_2O_6 using flux growth methods. A finely ground and homogenized mixture of Li_2CO_3 , Y_2O_3 and GeO_2 in the stoichiometry LiYGe_2O_6 was added to a high-temperature solvent (80 wt% Li_2MoO_4 and 20 wt% LiVO_3) in a ratio of educt to flux of 1 g:10 g. This starting material was placed in a platinum crucible, covered with a lid, heated in a chamber furnace to 1473 K, held for 24 h at this temperature and cooled to 1073 K at a rate of 1.8 K h^{-1} . After dissolution of the flux in hot distilled water, large thin tabular plates, probably of LiYGe_2O_6 , YVO_4 and $\text{Y}_2\text{Ge}_2\text{O}_7$ were obtained. The title compound forms large colourless grains of up to 2 mm, overgrown with the tabular LiYGe_2O_6 crystals.

Crystal data

$\text{Ge}_2\text{O}_7\text{Y}_2$	$Z = 4$
$M_r = 435.04$	Mo $K\alpha$ radiation
Tetragonal, $P4_32_12$	$\mu = 30.45$ mm^{-1}
$a = 6.8022(4)$ Å	$T = 295(2)$ K
$c = 12.3759(7)$ Å	$0.12 \times 0.07 \times 0.06$ mm
$V = 572.63(6)$ Å ³	

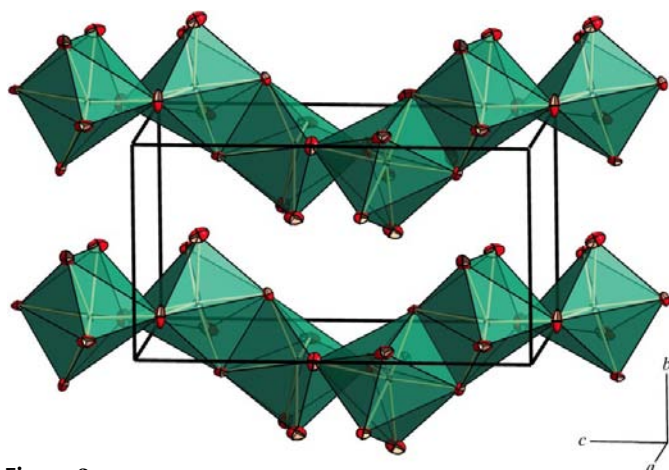


Figure 3

A polyhedral representation of the structure of $\text{Y}_2\text{Ge}_2\text{O}_7$ with only one helical chain of YO_7 polyhedra shown for clarity.

Data collection

Bruker SMART APEX diffractometer	6886 measured reflections
Absorption correction: numerical [via equivalents using X-SHAPE (Stoe & Cie, 1996)]	661 independent reflections
$T_{\min} = 0.091$, $T_{\max} = 0.18$	649 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	$\Delta\rho_{\text{max}} = 0.88 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.051$	$\Delta\rho_{\text{min}} = -0.71 \text{ e } \text{\AA}^{-3}$
$S = 1.19$	Absolute structure: Flack (1983), 228 Friedel pairs
661 reflections	Flack parameter: 0.0121 (16)
53 parameters	

Table 1

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

Y1—O2 ^v	2.211 (4)	Y1—O3 ⁱⁱ	2.552 (3)
Y1—O4	2.245 (3)	Ge1—O4	1.733 (3)
Y1—O4 ^{iv}	2.279 (3)	Ge1—O2	1.737 (3)
Y1—O3 ⁱ	2.284 (3)	Ge1—O1	1.769 (2)
Y1—O2 ⁱⁱ	2.373 (3)	Ge1—O3	1.780 (3)
Y1—O3 ⁱⁱⁱ	2.386 (3)		
O4—Ge1—O1	100.24 (16)	O2—Ge1—O3	95.32 (16)
O2—Ge1—O1	110.76 (19)	O1—Ge1—O3	115.08 (12)
O4—Ge1—O3	111.85 (16)		

Symmetry codes: (i) $y, x + 1, -z + 1$; (ii) $y - \frac{1}{2}, -x + \frac{1}{2}, z + \frac{1}{4}$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{5}{4}$; (iv) $y - \frac{1}{2}, -x + \frac{3}{2}, z + \frac{1}{4}$; (v) $y - 1, x + 1, -z + 1$.

Systematic extinction and intensity statistics yield two possible space groups, *viz.* $P4_12_12$ and $P4_32_12$. As the title compound appears to be isostructural with $\text{Eu}_2\text{Ge}_2\text{O}_7$, $\text{Tm}_2\text{Ge}_2\text{O}_7$ and $\text{Tb}_2\text{Ge}_2\text{O}_7$ at first glance, structure solution using direct methods (Sheldrick, 1997) was performed in the space group $P4_12_12$, yielding a structure model with one Y, one Ge and four independent O atoms, closely similar to that of, for example, $\text{Tb}_2\text{Ge}_2\text{O}_7$ (Geller & Gaines, 1987). The model refined down to 2.1% in R_1 ; however, the Flack (1983) parameter was 1.046 (16), indicative of the wrong absolute structure configuration. Refining the $P4_12_12$ model without the Flack parameter yielded $R_1 \approx 12\%$. Thus, the structure was inverted and the space group changed to $P4_32_12$, giving a Flack parameter of 0.0121 (16) for the correct absolute structure model presented here. During comparison with literature data, it became evident that the O2(y) coordinate of $\text{Eu}_2\text{Ge}_2\text{O}_7$ (Chiragov *et al.*, 1983) should read -0.0302 instead of $+0.0303$.

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 & Berndt, 1999); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3026). Services for accessing these data are described at the back of the journal.

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Table 2

Selected structural and polyhedral distortion parameters for the title compound compared with other lanthanide pyrogermanates.

	$\text{Y}_2\text{Ge}_2\text{O}_7^a$	$\text{Lu}_2\text{Ge}_2\text{O}_7^b$	$\text{Tm}_2\text{Ge}_2\text{O}_7^c$
$\langle\text{Ge—O}\rangle$ (\AA)	1.755	1.755	1.751
$\langle\text{O—O}\rangle$ (\AA)	2.858	2.856	2.850
Volume (\AA^3)	2.662	2.630	2.637
BLD ^g (%)	1.13	2.68	0.84
TAV ^h ($^\circ$)	110.20	138.43	117.09
TQE ⁱ	1.0275	1.0364	1.0292
Ge—O—Ge ($^\circ$)	134.86 (1)	130.0 (1)	135.48 (3)
$\langle R\text{—O}\rangle$ (\AA)	2.333	2.284	2.314
$\langle\text{O—O}\rangle$ (\AA)	3.116	3.052	3.092
Volume (\AA^3)	18.81	17.60	18.33
BLD ^g (%)	3.83	2.68	3.75
	$\text{Er}_2\text{Ge}_2\text{O}_7^d$	$\text{Tb}_2\text{Ge}_2\text{O}_7^e$	$\text{Eu}_2\text{Ge}_2\text{O}_7^f$
$\langle\text{Ge—O}\rangle$ (\AA)	1.749	1.754	1.766
$\langle\text{O—O}\rangle$ (\AA)	2.847	2.857	2.876
Volume (\AA^3)	2.634	2.657	2.707
BLD ^g (%)	0.46	1.10	1.07
TAV ^h ($^\circ$)	109.49	109.64	116.76
TQE ⁱ	1.0275	1.0278	1.0288
Ge—O—Ge ($^\circ$)	136.0 (4)	135.23 (4)	134.5 (3)
$\langle R\text{—O}\rangle$ (\AA)	2.324	2.360	2.383
$\langle\text{O—O}\rangle$ (\AA)	3.104	3.150	3.186
Volume (\AA^3)	18.623	19.484	20.160
BLD ^g (%)	4.15	3.76	4.31

(a) This study; (b) Palinka *et al.* (1995); (c) Stadnicka *et al.* (1990); (d) Smolin (1970); (e) Geller & Gaines (1987); (f) Chiragov *et al.* (1983); (g) bond-length distortion, $\text{BLD} = (100/n) \sum_{i=1}^n [|(X\text{—O})_i - \langle X\text{—O}\rangle| / \langle X\text{—O}\rangle]$, where n is the number of bonds, $(X\text{—O})_i$ is the central cation to oxygen length and $\langle X\text{—O}\rangle$ is the average cation–oxygen bond length (Renner & Lehmann, 1986); (h) tetrahedral angle variance, $\text{TAV} = \sum_{i=1}^n (\Theta_i - 109.47)^2 / 5$ (Robinson *et al.*, 1971), where Θ_i is the individual O—T—O tetrahedral angle; (i) tetrahedral quadratic elongation, $\text{TQE} = \sum_{i=1}^n (l_i/l_i)^2 / 4$, 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_i (Robinson *et al.*, 1971).

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