$Y_{0.76}Ho_{0.24}FeGe_2O_7$: a new member of thortveitite-like layered compounds

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$Y_{0.76}Ho_{0.24}FeGe_2O_7$ (yttrium holmium iron digermanate) was synthesized by solid-state reaction at 1573 K. This thortveitite-like compound presents a crystallographic group–subgroup isotranslational (*klassengleiche*) relation with some other pyrogermanates, such as $FeInGe_2O_7$, $In_{1.08}Gd_{0.92}Ge_2O_7$ and $InYGe_2O_7$, which are configurationally isotypic with the $Sc_2Si_2O_7$ thortveitite structure first reported by Zachariasen [(1930). *Z. Kristallogr.* **73**, 1–6]. Holmium cations share with yttrium the 4*f* Wyckoff position at the center of a seven-coordinated pentagonal bipyramid, while Fe atoms also occupy one site with Wyckoff position 4*f* at the center of the octahedron. All these sites have the point symmetry C_1. Two types of Ge_2O_7 diorthogroups with point symmetry C_{1h} are present in the structure, each one of them defining a layer type which alternates with the other. These diorthogroups have their tetrahedral groups in an eclipsed conformation.

Related literature

The method of preparation was based on work published by Cascales *et al.* (1998*b*). For related structures, see: Zachariasen (1930); Cascales *et al.* (1998*a*,*b*, 2002); Bucio *et al.* (2001); Redhammer *et al.* (2007).

Experimental

Crystal data

$Y_{0.76}Ho_{0.24}FeGe_2O_7$
$M_r = 420.17$
Monoclinic, $P2_1/m$
$a = 9.6496\ (2)$ Å
$b = 8.5073\ (2)$ Å
$c = 6.6712\ (2)$ Å
$\beta = 100.621\ (1)°$
$V = 538.27\ (2)$ Å³

$Z = 4$
Cu $K\alpha$ radiation
$T = 295$ K
Specimen shape: flat sheet
$20 \times 20 \times 0.2$ mm
Specimen prepared at 1573 K
Particle morphology: spherical, brown

Data collection

Bruker Advance D8 diffractometer
Specimen mounting: packed powder sample container
Specimen mounted in reflection mode

Scan method: step
$2\theta_{min} = 10$, $2\theta_{max} = 80.0°$
Increment in $2\theta = 0.02°$

Refinement

$R_p = 0.07$
$R_{wp} = 0.09$
$R_{exp} = 0.06$
$R_B = 0.03$
$S = 1.53$
Wavelength of incident radiation: 1.54175 Å

Profile function: pseudo-Voigt modified by Thompson *et al.* (1987)
843 reflections
60 parameters

Table 1
Selected geometric parameters (Å, °).

Ge1—O4[i]	1.70 (3)	Ge3—O3[v]	1.77 (4)
Ge1—O9[ii]	1.82 (3)	Ge3—O5	1.82 (3)
Ge1—O10	1.78 (3)	Ge3—O5[iv]	1.82 (3)
Ge1—O10[iii]	1.78 (3)	Ge3—O6[vi]	1.76 (6)
Ge2—O1	1.69 (3)	Ge4—O2[vii]	1.67 (3)
Ge2—O1[iv]	1.69 (3)	Ge4—O3[vii]	1.73 (4)
Ge2—O4	1.98 (3)	Ge4—O7	1.87 (3)
Ge2—O8	1.78 (4)	Ge4—O7[iv]	1.87 (3)
Ge1[viii]—O4—Ge2	127.7 (16)	Ge3[ix]—O3—Ge4[vi]	165 (2)

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

Data collection: *DIFFRAC/AT* (Siemens, 1993); cell refinement: *DICVOL91* (Boultif & Louër, 1991); data reduction: *FULLPROF* (Rodríguez-Carvajal, 2006); program(s) used to solve structure: coordinates taken from an isotypic compound (Cascales *et al.*, 2002) show [/query]>; program(s) used to refine structure: *FULLPROF* ; molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *ATOMS*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2109).

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supporting information

$Y_{0.76}Ho_{0.24}FeGe_2O_7$: a new member of thortveitite-like layered compounds

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S1. Comment

The crystal structure of the original thortveitite was first reported by Zachariasen (1930) and has the formula $Sc_2Si_2O_7$. In this silicate, the substitution of silicon has given rise to germanates, phosphates, arsenates and vanadates which present layered structures.

The ionic substitution from Si to Ge and Sc to trivalent metals and rare earths in thortveitite, give often germanates with thortveitite-like crystal structure $RMGe_2O_7$, where R and M represent cations of rare earths, transition metals, divalent or trivalent elements in octahedral coordination. The frameworks of these phases are built up from corner-sharing octahedra along ab planes forming a hexagonal disposition on layers interspersed with layers of Ge_2O_7 groups in staggered conformation (in Fig. 1a the octahedra appear in dark cyan, while the Ge_2O_7 group in yellow color).

Some ionic substitutions give rise to seven-coordinated cations occupying the half of octahedral sites in the thortveitite structure. In such case, the generalized formula can be written as MRX_2O_7 where X_2O_7 is the same diorthogroup mentioned before presenting almost the same features as in thortveitite. The octahedral sites split in two new sites: half for cation M and other half for cation R, such as the cases for R = Y, Tb–Yb (Cascales *et al.*, 1998*a*,*b*, 2002). M remains with octahedral coordination while R changes its coordination to seven. In the present work we present the crystal structure of the new compound $Y_{1-x}Ho_xFeGe_2O_7$ with $x = 0.24$.

Fig. 1b show the crystal structure of $Y_{0.76}Ho_{0.24}FeGe_2O_7$ in which the bridging O atoms at the middle of the Ge_2O_7 diorthogroup are displaced up (u) or down (d) along a direction normal to the cb plane. RO_7 polyhedra are connected alternately by either a vertex or an edge into chains along the b axis, Fig. 1b (medium slate blue colored polyhedra). In the same direction only isolated pairs of associated MO_6 octahedra exist, as can be seen in the same figure (light gray octahedra). Flattened chains of RO_7 polyhedra (in yellow) are linked in the c direction through pairs of MO_6 octahedra with which they share edges forming layers running parallel to the bc crystal plane.

The most important feature in the structure previously described is the presence of Ge—O—Ge angles in the Ge_2O_7 group different from 180° giving rise to seven-coordinated cations in a half of the octahedral sites in the idealized thortveitite structure. The results of the Rietveld refinement established the presence of two crystalline phases for the method of synthesis used. The quantitative analysis gave 91.2 (8)% for $Y_{0.76}Ho_{0.24}FeGe_2O_7$ and 8.8 (3)% for $Y_2Ge_2O_7$. With these results, the chemical reaction compatible with the quantitative analysis is:

$$4Y_2O_3 + Ho_2O_3 + 5Fe_2O_3 + 30GeO_2 \rightarrow 8.43Y_{0.76}Ho_{0.24}FeGe_2O_7 + 0.79Y_2Ge_2O_7 + 11.56\ GeO_2 + 0.78Fe_2O_3.$$
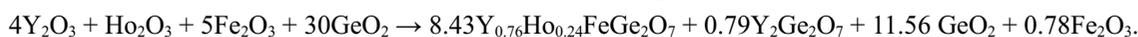
S2. Experimental

The reactive mixture was prepared from Y_2O_3 (Aldrich.99.99%), Ho_2O_3 (Aldrich.99.9%), Fe_2O_3 (Aldrich.99.99%) and GeO_2 (CERAC 99.999%) according to the method reported by Cascales *et al.* (1998*b*). This mixture was first powdered using an agate mortar; and then was heated in air in a tube furnace at 1573 K for 5 d with intermediate regrinding. At the end of the reaction, some vitreous phase impregnated and segregated at the bottom of the crucible was attributed to the

presence of amorphous GeO_2. Small amount of Fe_2O_3 was also detected as trace phase. The characterization of the bulk material by conventional X-ray powder diffraction data indicated two phases well crystallized. One of them showed reflections that were explained matching the isostructural phase $YFeGe_2O_7$ (PDF 01-072-6099) and the other one was identified as $Y_2Ge_2O_7$ (PDF 38-288).

S3. Refinement

The structural model for $YFeGe_2O_7$ (ICSD 95935) was taken for start the Rietveld refinement of $Y_{1-x}Ho_xFeGe_2O_7$ with $x =$ 1/5, while for the secondary phase, the data used for $Y_2Ge_2O_7$ (ICSD 240989) was those reported by Redhammer *et al.* (2007). The Rietveld refinement was made using the Fullprof program (Rodríguez-Carvajal, 2006). A pseudo-Voigt function modified by Thompson *et al.* (1987) was chosen to generate the peak shape of the diffraction reflections. The following parameters were refined: zero point and scale factors, cell parameters, half-width profile parameters, overall temperature factors, preferred orientation, atomic coordinates, and asymmetries. For the $Y_2Ge_2O_7$ phase no preferred orientation was considered, and the atomic coordinates were fixed to their starting values and an overall temperature factor was considered. The background was refined first by mean of a linear interpolation between 55 background points with adjustable heights. At the end of the refinement, the values for all of these heights of the background were fixed. The final Rietveld refinement of conventional diffraction pattern is shown in Figure 21.
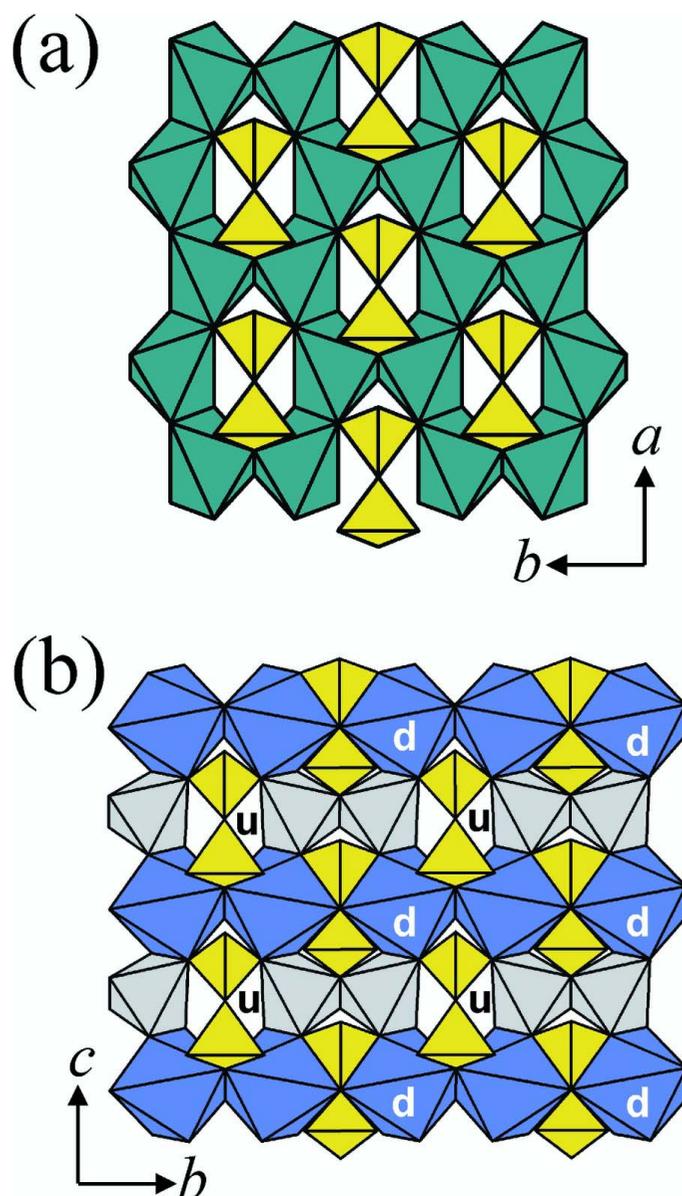
Figure 1

(*a*) View of a layer in the thortveitite structure (*ab* projection). Diorthogroups X_2O_7 are represented as yellow tetrahedra and MO_6 octahedra in dark cyan. (*b*) View of thortveitite-like structure of $Y_{0.76}Ho_{0.24}FeGe_2O_7$ (*ac* projection). Diorthogroups Ge_2O_7 are represented as yellow tetrahedra, while FeO_6 octahedra appear in light gray, and $(Y,Ho)O_7$ polyhedra (medium slate blue). The bridging O atoms of Ge_2O_7 groups are displaced up (*u*) and down (*d*) normal to the *cb* plane from its original position in thortveitite.
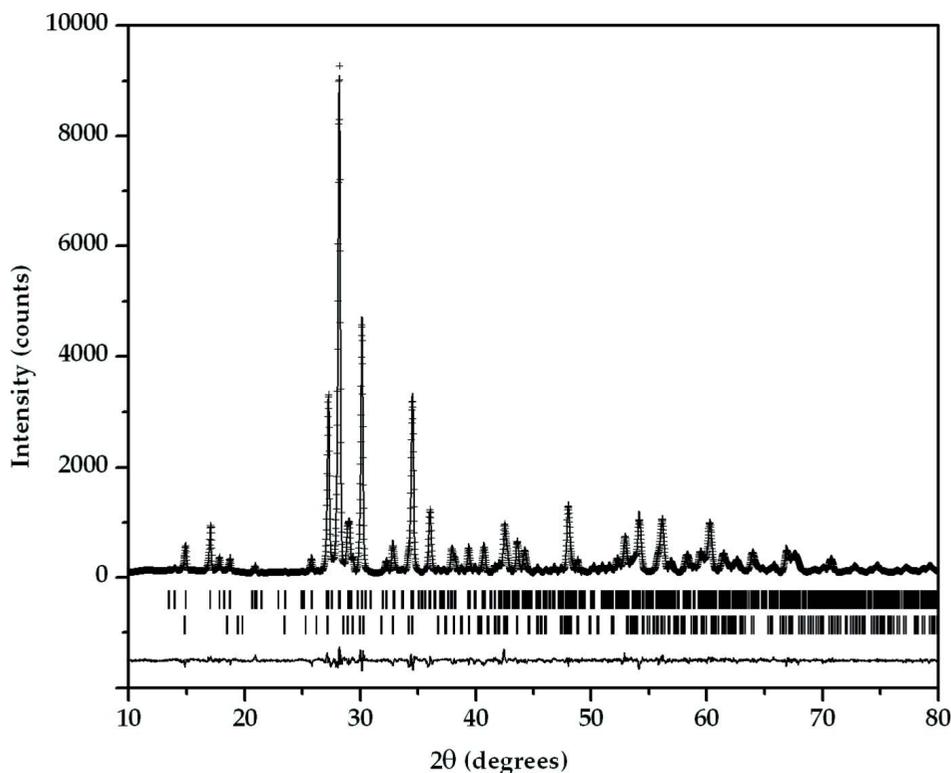
Figure 2

Rietveld refinement for $Y_{0.76}Ho_{0.24}FeGe_2O_7$ X-ray diffraction data. Observed (crosses), calculated (solid line) and difference (bottom trace) plots are represented; vertical marks correspond to the allowed Bragg reflections for $Y_{0.76}Ho_{0.24}FeGe_2O_7$ (top) and $Y_2Ge_2O_7$ (bottom).

yttrium holmium iron digermanate

Crystal data

$Y_{0.76}Ho_{0.24}FeGe_2O_7$	$Z = 4$
$M_r = 420.17$	$F(000) = 768.0$
Monoclinic, $P2_1/m$	$D_x = 5.186$ Mg m^{-3}
Hall symbol: -P 2yb	Cu $K\alpha$ radiation, $\lambda = 1.54175$ Å
$a = 9.6496$ (2) Å	$T = 295$ K
$b = 8.5073$ (2) Å	brown
$c = 6.6712$ (2) Å	flat sheet, 20×20 mm
$\beta = 100.621$ (1)°	Specimen preparation: Prepared at 1573 K
$V = 538.27$ (2) Å^3	

Data collection

Bruker Advance D8 diffractometer	Specimen mounting: packed powder sample container
Radiation source: sealed X-ray tube, Cu Kα	Data collection mode: reflection
Graphite monochromator	Scan method: step
	$2\theta_{min} = 10°$, $2\theta_{max} = 80.00°$, $2\theta_{step} = 0.02°$

Refinement

Least-squares matrix: full with fixed elements per cycle	Profile function: pseudo-Voigt modified by Thompson *et al.* (1987)
$R_p = 0.07$	60 parameters
$R_{wp} = 0.09$	Weighting scheme based on measured s.u.'s
$R_{exp} = 0.06$	$(\Delta/\sigma)_{max} = 0.02$
$R_{Bragg} = 0.03$	Background function: linear interpolation between a set background points with refinable heights
$R(F^2) = 0.03$	
$\chi^2 = 2.341$	
3501 data points	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Y	0.7521 (11)	0.5406 (3)	0.7509 (10)	0.0120 (5)	0.76000
Ho	0.7521 (11)	0.5406 (3)	0.7509 (10)	0.0120 (5)	0.24000
Fe	0.7467 (15)	0.4473 (5)	0.2648 (16)	0.0120 (5)	
Ge1	0.5263 (14)	0.75000	0.0459 (17)	0.0120 (5)	
Ge2	0.5471 (13)	0.25000	0.4897 (14)	0.0120 (5)	
Ge3	0.9469 (13)	0.25000	0.0252 (15)	0.0120 (5)	
Ge4	0.0310 (13)	0.25000	0.5427 (18)	0.0120 (5)	
O1	0.627 (3)	0.427 (3)	0.499 (5)	0.0120 (5)	
O2	0.874 (4)	0.25000	0.389 (4)	0.0120 (5)	
O3	0.966 (3)	0.25000	0.766 (5)	0.0120 (5)	
O4	0.590 (3)	0.25000	0.792 (4)	0.0120 (5)	
O5	0.845 (3)	0.070 (3)	0.028 (4)	0.0120 (5)	
O6	0.130 (6)	0.25000	0.119 (6)	0.0120 (5)	
O7	0.150 (3)	0.083 (3)	0.502 (3)	0.0120 (5)	
O8	0.375 (5)	0.25000	0.334 (5)	0.0120 (5)	
O9	0.606 (4)	0.25000	0.186 (5)	0.0120 (5)	
O10	0.640 (3)	0.584 (3)	0.070 (3)	0.0120 (5)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
?	?	?	?	?	?	?

Geometric parameters (Å, º)

Fe—O1	2.11 (4)	Ge1—O10	1.78 (3)
Fe—O2	2.15 (2)	Ge1—O10[vi]	1.78 (3)
Fe—O5[i]	1.99 (3)	Ge2—O1	1.69 (3)
Fe—O7[ii]	2.04 (2)	Ge2—O1[i]	1.69 (3)
Fe—O9	2.16 (2)	Ge2—O4	1.98 (3)
Fe—O10	1.90 (2)	Ge2—O8	1.78 (4)
Ho—O1	2.11 (3)	Ge3—O3[vii]	1.77 (4)
Ho—O4	2.96 (2)	Ge3—O5	1.82 (3)
Ho—O5[iii]	2.12 (3)	Ge3—O5[i]	1.82 (3)
Ho—O6[ii]	2.20 (3)	Ge3—O6[viii]	1.76 (6)

Ho—O7[ii]	2.11 (3)	Ge4—O2[ix]	1.67 (3)
Ho—O8[ii]	2.18 (3)	Ge4—O3[ix]	1.73 (4)
Ho—O10[iv]	2.59 (3)	Ge4—O7	1.87 (3)
Ge1—O4[ii]	1.70 (3)	Ge4—O7[i]	1.87 (3)
Ge1—O9[v]	1.82 (3)		
O1—Ho—O4	57.2 (1)	O1—Ho—O8[ii]	87.3 (2)
O1—Ho—O5[iii]	125 (2)	O1—Ho—O10[iv]	117.1 (2)
O1—Ho—O6[ii]	149 (2)	Ge1[x]—O4—Ge2	127.7 (16)
O1—Ho—O7[ii]	73.6 (2)	Ge3[iv]—O3—Ge4[viii]	165 (2)

Symmetry codes: (i) x, $-y+1/2$, z; (ii) $-x+1$, $y+1/2$, $-z+1$; (iii) x, $-y+1/2$, $z+1$; (iv) x, y, $z+1$; (v) $-x+1$, $y+1/2$, $-z$; (vi) x, $-y+3/2$, z; (vii) x, y, $z-1$; (viii) $x+1$, y, z; (ix) $x-1$, y, z; (x) $-x+1$, $y-1/2$, $-z+1$.