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$In_{1.06}Ho_{0.94}Ge_2O_7$: a thortveitite-type compound

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A new indium holmium digermanate, $In_{1.06}Ho_{0.94}Ge_2O_7$, with a thortveitite-type structure, has been prepared as a polycrystalline powder material by high-temperature solid-state reaction. This new compound crystallizes in the monoclinic system (space group *C*2/*c*, No. 15). The structure was characterized by Rietveld refinement of powder laboratory X-ray diffraction data. The In^{3+} and Ho^{3+} cations occupy the same octahedral site, forming a hexagonal arrangement on the *ab* plane. In their turn, the hexagonal arrangements of $(In/Ho)O_6$ octahedral layers are held together by sheets of isolated diortho groups comprised of double tetrahedra sharing a common vertex. In this compound, the Ge_2O_7 diortho groups lose the ideal D_{3d} point symmetry and also the C_{2h} point symmetry present in the thortveitite diortho groups. The Ge—O—Ge angle bridging the diortho groups is 160.2 (3)°, compared with 180.0° for Si—O—Si in thortveitite ($Sc_2Si_2O_7$). The characteristic mirror plane in the thortveitite space group (*C*2/*m*, No. 12) is not present in this new thortveitite-type compound and the diortho groups lose the C_{2h} point symmetry, reducing to C_2.

Comment

Previous work on a series of isomorphous germanates $MRGe_2O_7$ (where *M* is In, Mn, Fe, Y, Sc, Ga or Al, and *R* is a rare earth) has included compounds such as $FeInGe_2O_7$ (Bucio *et al.*, 2001) and $InYGe_2O_7$ (Juarez-Arellano, Bucio *et al.*, 2002), described by the space group *C*2/*m* (No. 12) and adopting the thortveitite structure, $FeRGe_2O_7$ (where *R* is La, Pr, Nd or Gd; Bucio *et al.*, 1996) and $NdAlGe_2O_7$ (Jarchow *et al.*, 1985), taking space group $P2_1/c$ (No. 14), and $FeRGe_2O_7$ (*R* is Y or Tb–Yb; Cascales *et al.*, 1998), $GdMnGe_2O_7$ and $EuMnGe_2O_7$ (Taviot-Gueho *et al.*, 1999; Juarez-Arellano *et al.*, 2001), with space group *A*222 (No. 21). Interesting optical, electrical and magnetic properties have been reported in these kinds of compounds.

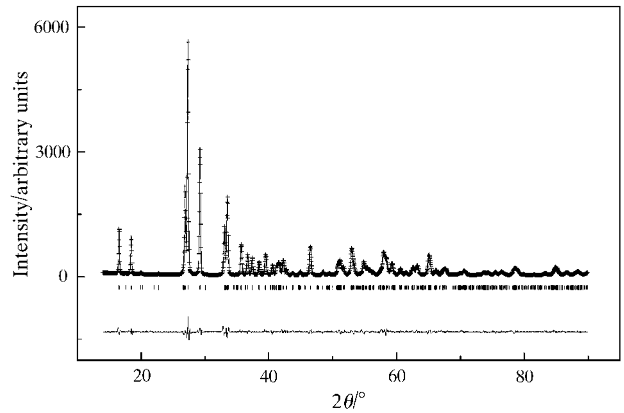

Figure 1
The observed (crosses), calculated (solid line) and difference (at the bottom) X-ray powder diffraction profile for $In_{1.06}Ho_{0.94}Ge_2O_7$ at room temperature. Vertical marks correspond to the position of the allowed Bragg reflections.

In recent years, compounds with rare earth cations (especially Gd^{3+}, Tb^{3+}, Eu^{3+} and Ho^{3+}) have been developed and employed as scintillators for radiation detectors used in medical diagnostics, industrial inspection, dosimetry, nuclear medicine and high-energy physics. In each application, the scintillator is the primary radiation sensor that emits light or scintillates when it is struck by high-energy photons (Greskovich & Duclos, 1997). Polycrystalline ceramic scintillators are a relatively new class of materials developed for quantitative detection accuracy. Ceramic scintillators have been attracting increasing attention because their complex compositions, which cannot be grown by single-crystal methods, can be synthesized by relatively inexpensive ceramic processes.

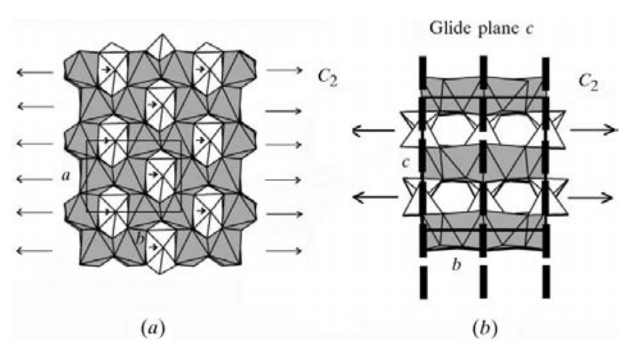

Figure 2
A projection of $In_{1.06}Ho_{0.94}Ge_2O_7$ on the *ab* plane, showing the honeycomb-like arrangement of $(In/Ho)O_6$ octahedra (in dark grey). (*a*) The Ge_2O_7 diortho groups (light grey) link at three points to the hexagonal rings of octahedra. The displacement of bridging O atoms to the right-hand side (black arrows) is clearly seen, changing the C_{2h} symmetry of the Ge_2O_7 diortho groups to C_2. (*b*) $(In/Ho)O_6$ octahedral layers (dark grey) are held together alternately along the *c* axis by sheets of isolated Ge_2O_7 diortho groups (in light grey).

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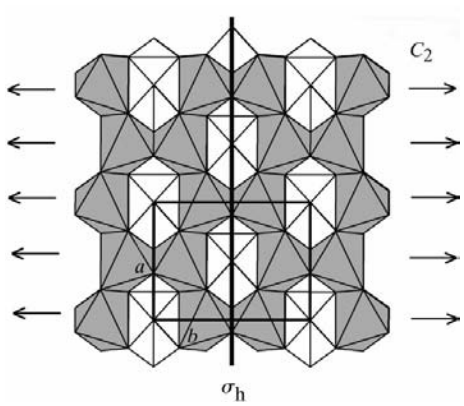

Figure 3
A projection of the $Sc_2Si_2O_7$ thortveitite structure on the *ab* plane.

Recently, we have reported the crystal structure of two new germanates with remarkable luminescence, namely $In_{1.08}Gd_{0.96}Ge_2O_7$ (space group *C*2/*m*, No. 12; Juarez-Arellano, Rosales *et al.*, 2002), and $InTbGe_2O_7$ (space group *C*2/*c*, No. 15; Juarez-Arellano *et al.*, 2003). Both compounds are potentially useful scintillators. Bearing in mind our previous results, we have been trying to expand the search for scintillation to include thousands of compounds that are not yet available as crystals (Derezo *et al.*, 1990; Moses *et al.*, 1997). The present work is devoted to the synthesis and crystal structure characterization of a new holmium-based compound having the stoichiometric formula $In_{1.06}Ho_{0.94}Ge_2O_7$. The first thortveitite-type compound reported with the space group *C*2/*c* (No. 15) was the phosphate $Cu_2P_2O_7$ (Robertson & Calvo, 1967). Since then, just four laminar compounds have been published (Bucio *et al.*, 2003) with this symmetry, namely $Zn_2V_2O_7$ (Gopal & Calvo, 1973), $Cu_2V_2O_7$ (Mercurio-Lavaud & Frit, 1973), $Al_2Ge_2O_7$ (Agafonov *et al.*, 1986) and $InTbGe_2O_7$ (Juarez-Arellano *et al.*, 2003).

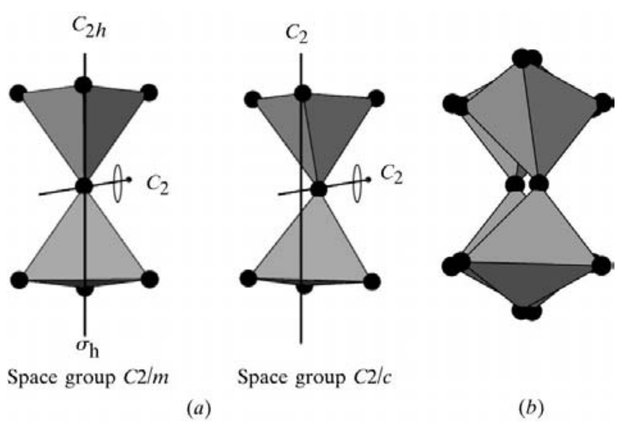

Figure 4
(*a*) A comparison between the C_{2h} point symmetry of the Ge_2O_7 diortho groups in the thortveitite structure and the C_2 point symmetry in the thortveitite-type structure. (*b*) Contiguous sheets of Ge_2O_7 diortho groups have their bridging O atoms displaced in opposing directions, generating the *c*-glide plane.

The title structure is built up of hexagonally arranged $(In/Ho)O_6$ octahedral layers, which are separated by intermediate layers of Ge_2O_7 diortho groups. The average (In,Ho)—O distance of 2.27 Å, evaluated over the unique octahedral sites occupied by both In and Ho atoms, is very close to the sum of the ionic radii, $r(In^{3+}/Ho^{3+}) + r(O^{2-})$ = 2.251 Å, where $r(In^{3+}/Ho^{3+})$ is the average value of the In^{3+} and Ho^{3+} ionic radii. The values used for these calculations were 0.80, 0.901 and 1.40 Å, for $r(In^{3+})$, $r(Ho^{3+})$ and $r(O^{2-})$, respectively (Shannon, 1976). The Ge—O distances range from 1.57 to 1.80 Å (mean 1.68 Å) and the GeO_4 tetrahedra are a little more irregular than those encountered in the $InTbGe_2O_7$ compound [mean 1.72 (2) Å; Juarez-Arellano *et al.*, 2003]. In the latter case, the average (In/Tb)—O distance for the $(In/Tb)O_6$ octahedra is 2.24 (2) Å, which is in agreement with the sum of the ionic radii of In/Tb and O atoms.

In the ideal thortveitite structure, the diortho groups possess C_{2h} point symmetry. However, with the incorporation of Ho^{3+}, distortions reduce the coordination number and the symmetry is lowered to C_2. The twofold symmetry is not broken because the bridging O atoms are displaced in a parallel direction with respect to the twofold symmetry axis. Contiguous sheets of diortho groups have their bridging O atoms displaced in opposing directions, generating a doubled *c* axis with a *c*-glide plane replacing the mirror plane of thortveitite. The distortions reduce the diortho group Ge—O—Ge bridging angle from 180.0 to 160.2 (3)°.

Experimental

$In_{1.06}Ho_{0.94}Ge_2O_7$ was prepared as a polycrystalline powder material by solid-state reaction from a stoichiometric mixture of analytical grade Ho_2O_3, GeO_2 and In_2O_3. The sample was ground and heated in air at 1423 K for 5 d with intermediate regrinding. The standard X-ray powder diffraction analysis indicated that the final sample was well crystallized and appeared completely free of secondary crystalline phases. The elemental composition was determined by Rutherford backscattering spectrometry (RBS), following the procedure reported by Bucio *et al.* (2001). The stoichiometric values for In, Ho, Ge and O were 1.12, 1.0, 2.6 and 7.8 (±7%), respectively. The amounts of Ge and O are slightly higher, owing to the presence of amorphous GeO_2.

Crystal data

$In_{1.06}Ho_{0.94}Ge_2O_7$
M_r = 536.97
Monoclinic, *C*2/*c*
a = 6.8348 (2) Å
b = 8.8863 (3) Å
c = 9.8177 (3) Å
β = 101.789 (1)°
V = 583.71 (3) Å^3
Z = 4
D_x = 6.110 (2) Mg m^{-3}
Cu $K\alpha$ radiation
μ = 67.30 mm^{-1}
T = 295 K
Specimen shape: irregular
20 × 20 × 0.2 mm
Specimen prepared at 1423 K
Particle morphology: heterogeneous particles with sizes 1–5 µm, white

Data collection

Siemens D5000 diffractometer
Specimen mounting: packed powder sample container
Specimen mounted in reflection mode
T = 295 K
$2\theta_{min}$ = 14, $2\theta_{max}$ = 90°
Increment in 2θ = 0.02°

Refinement

Refinement on I_{net}
R_p = 0.079
R_{wp} = 0.111
R_{exp} = 0.078
R_B = 0.030
S = 1.43
$2\theta_{min}$ = 14, $2\theta_{max}$ = 90°
Increment in 2θ = 0.02°
Wavelength of incident radiation: 1.540562, 1.544390 Å
Profile function: pseudo-Voigt modified by Thompson *et al.* (1987)
624 reflections
36 parameters
$(\Delta/\sigma)_{max}$ = 0.01
Preferred orientation correction: none

Table 1
Selected geometric parameters (Å, °).

In—O2^{i}	2.17 (2)	In—O4^{vi}	2.33 (2)
In—O2^{ii}	2.40 (2)	Ge—O1	1.718 (4)
In—O3^{iii}	2.16 (2)	Ge—O2	1.63 (1)
In—O3^{iv}	2.30 (2)	Ge—O3	1.79 (2)
In—O4^{v}	2.28 (2)	Ge—O4	1.56 (2)
O2^{i}—In—O2^{ii}	81.3 (9)	O1—Ge—O2	102.6 (3)
O2^{i}—In—O3^{iii}	84.0 (14)	O1—Ge—O3	100.9 (15)
O2^{i}—In—O3^{iv}	90.6 (12)	O1—Ge—O4	112.1 (17)
O2^{i}—In—O4^{v}	159.0 (16)	O2—Ge—O3	117.4 (18)
O2^{i}—In—O4^{vi}	77.1 (11)	Ge—O1—Ge^{iii}	167.0 (3)

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

The powder diffraction pattern was indexed using the *TREOR* program (Werner *et al.*, 1985). Following the criteria of Cruickshank *et al.* (1962), we consider the novel compound $In_{1.06}Ho_{0.94}Ge_2O_7$ to be a thortveitite-type structure described by the space group *C*2/*c* (No. 12). The Rietveld method was used to refine the crystal structure using initial parameters obtained from the $Cu_2P_2O_7$ thortveitite-type structure (ICSD card No. 14369, structural data from Robertson & Calvo, 1967). A pseudo-Voigt function modified by Thompson *et al.* (1987) was chosen to model the shape of the diffraction peaks. A total of 36 independent parameters were refined, including the zero point, scale factor, five background polynomial coefficients, unit-cell parameters, half-width and asymmetry parameters for the peak shape, atomic coordinates, occupation and isotropic atomic displacement parameters.

Data collection: *DIFFRAC/AT* (Siemens, 1993); cell refinement: *DICVOL*91 (Boultif & Louër, 1991); program(s) used to refine structure: *FULLPROF* (Rodríguez-Carvajal, 1990); molecular graphics: *ATOMS* (Dowty, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1037). Services for accessing these data are described at the back of the journal.

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