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$In_{1.08}Gd_{0.92}Ge_2O_7$: a new member of the thortveitite family

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Indium gadolinium digermanium heptaoxide, $In_{1.08}Gd_{0.92}Ge_2O_7$, with a thortveitite-type structure, has been prepared as a polycrystalline powder material by a high-temperature solid-state reaction. As in the mineral thortveitite, the crystal structure belongs to the monoclinic system, with space group *C*2/*m* (No. 12). The precise structural parameters were obtained by applying the Rietveld method of refinement to the X-ray powder diffraction data. This layered structure presents, on one side, a honeycomb-like arrangement of the unique octahedral site, which is occupied randomly by In and Gd atoms, and, on the other side, sheets of isolated Ge_2O_7 diortho-groups made up of double tetrahedra sharing a common vertex and displaying C_{2h} point symmetry. This compound showed a remarkable photoluminescence effect when it was irradiated with the X-ray beam during the X-ray diffraction measurements, and with the α beam during the Rutherford back-scattering spectrometry experiments employed to analyze the chemical stoichiometry.

Comment

Since Zachariasen (1930) published his work on the $Sc_2Si_2O_7$ thortveitite structure, many compounds belonging to this structure type have been synthesized and their complete and precise structural data reported. In 1962, as a result of a reinvestigation of the crystal structure of thortveitite, Cruickshank *et al.* (1962) considered the possibility of exchanging Sc^{3+} with other cations, such as Y^{3+} and Fe^{3+}, to observe the effects that this might have on the crystal symmetry, specifically on the point symmetry shown by the Ge_2O_7 diortho-group and the presence or otherwise of a mirror plane, which is the difference between *C*2 and *C*2/*m* as possible space groups for thortveitite.

In subsequent years, many compounds have been synthesized which presented the thortveitite structure or variations of it, namely $Sm_2Si_2O_7$ (Smolin *et al.*, 1970), $Y_2Si_2O_7$ (Batalieva & Pyatenko, 1971), $Pr_2Si_2O_7$ (Felshe, 1971), $In_2Si_2O_7$ (Reid *et al.*, 1977; Gaewdang *et al.*, 1994) and $Gd_2Si_2O_7$ (Smolin & Shepelev, 1967). In the same way, the Si atom has been exchanged for Ge, giving rise to the pyrogermanate compounds $Er_2Ge_2O_7$ (Smolin, 1970), $Gd_2Ge_2O_7$ (Smolin *et al.*, 1971), $Eu_2Ge_2O_7$ (Chigarov *et al.*, 1983) and so on. Many of these germanium-based compounds also retained the thortveitite structure, but some of them changed their crystal symmetry.

Recently, the crystal structure of iron indium digermanate, $FeInGe_2O_7$, has been reported (Bucio *et al.*, 2001), which also has the typical thortveitite layered structure. This compound belongs to a new class of monoclinic germanates, of general stoichiometric formula $MRGe_2O_7$, where *M* and *R* represent trivalent metals (such as Al, Ga or Fe) and rare earth ions, respectively. Among these compounds can be found crystal symmetries described by the space groups *C*2/*m* (No. 12), as in thortveitite, *C*2/*c* (No. 15), represented by $InTbGe_2O_7$ (Juarez-Arellano *et al.*, 2002), *P*2$_1$/*c* (No. 14), as in $FeRGe_2O_7$ (*R* is La, Pr, Nd or Gd; Bucio *et al.*, 1996), and *P*2$_1$/*m* (No. 11), as in $FeRGe_2O_7$ (*R* is Y or Tb/Yb; Cascales *et al.*, 1998).

This kind of compound has been of great interest in laser crystal physics. For instance, the incorporation of R^{3+} activators into single-centred hosts, up to full substitution of all cations, gives the possibility of obtaining so-called self-activated crystals. Other recently reported layered compounds with interesting optical responses are $GdMnGe_2O_7$ (Taviot-Gueho *et al.*, 1999) and $MnEuGe_2O_7$ (Juarez-Arellano *et al.*, 2001), these being the only cases in which an orthorhombic symmetry (space group *A*222, No. 21) can be found.

In recent years, compounds with rare earth cations, especially Gd^{3+}, have been developed and employed as scintillators for applications in a variety of fields, such as medical imaging, high-energy physics and space-borne γ-ray astronomy (Moses *et al.*, 1997; Yasunobu *et al.*, 2001). The present work is devoted to the synthesis and crystal structure characterization of a new gadolinium-based compound having the formula

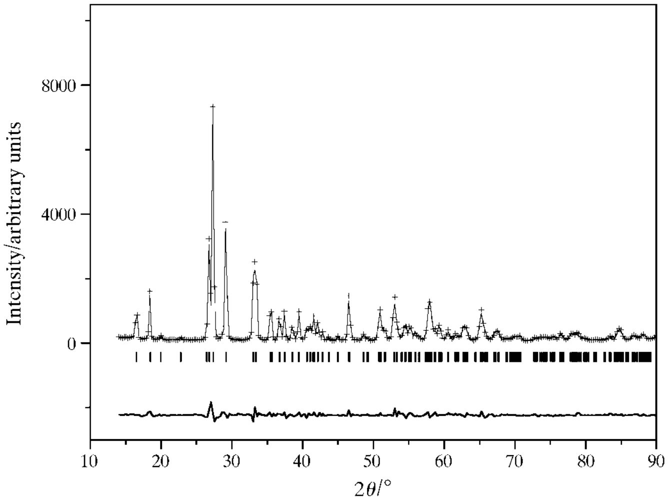

Figure 1
The observed (+++) and calculated (solid line) X-ray powder diffraction profiles for $In_{1.08}Gd_{0.92}Ge_2O_7$ at room temperature. The difference profile is given at the bottom. The vertical marks correspond to the positions of the allowed Bragg reflections.

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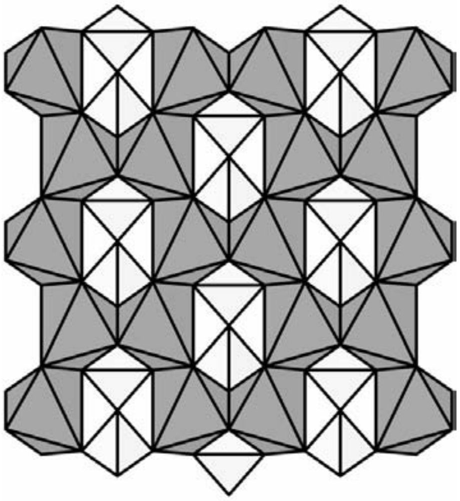

Figure 2
The projection of the $In_{1.08}Gd_{0.92}Ge_2O_7$ structure on the *ab* plane, showing the honeycomb-like arrangement of InO_6 (or GdO_6) octahedra (grey). The Ge_2O_7 diortho-groups (white) are linked to the hexagonal rings of octahedra at three points.

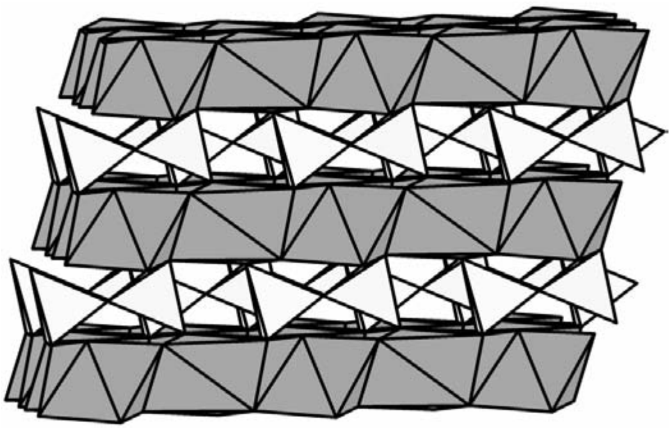

Figure 3
The RO_6 octahedral layers, where *R* represents In or Gd atoms, are held together alternately along the *c* axis by sheets of isolated Ge_2O_7 diortho-groups. The shading convention is the same as in Fig. 2.

$In_{1.08}Gd_{0.92}Ge_2O_7$. This allowed us to study and understand the optical and other physical properties of this layered compound.

The title structure is built up of layers of InO_6 and GdO_6 octahedra in a nearly hexagonal arrangement, which are kept apart by Ge_2O_7 pyrogermanate groups presenting C_{2h} point-group symmetry. The average (In/Gd)—O distance of 2.252 Å, evaluated over the unique octahedral site occupied by both In and Gd atoms, is very close to the sum of the ionic radii; $r(In^{3+}/Gd^{3+}) + r(O^{2-}) = 2.269$ Å, where $r(In^{3+}/Gd^{3+})$ is the average of the ionic radii for In^{3+} and Gd^{3+}. The values used for these calculations were 0.80, 0.938 and 1.40 Å for $r(In^{3+})$, $r(Gd^{3+})$ and $r(O^{2-})$, respectively (Shannon, 1976).

The Ge—O distances in $In_{1.08}Gd_{0.92}Ge_2O_7$ are in the range 1.695–1.703 Å (average 1.698 Å). Therefore, the GeO_4 tetrahedra are approximately regular, more than those described for the $In_2Ge_2O_7$ compound reported by Gaewdang *et al.* (1994). In this last case, the average In—O distance for the InO_6 octahedra is 2.177 Å, which is in agreement with the sum of the ionic radii of In and O, and lower than the corresponding value of 2.252 Å for the $In_{1.08}Gd_{0.92}Ge_2O_7$ compound reported here. All these findings are consistent with the addition of Gd.

Experimental

$In_{1.08}Gd_{0.92}Ge_2O_7$ was prepared as a polycrystalline powder material by solid-state reaction from a stoichiometric mixture of analytical grade Gd_2O_3, GeO_2 and In_2O_3. The sample was ground and heated in air at 1423 K for 5 d with intermediate regrindings. 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 previously reported by Bucio *et al.* (2001). The stoichiometric values for In, Gd, Ge and O elements were 1.0, 1.0, 2.6 and 7.9% (±7%), respectively. The amounts of Ge and O are slightly high because of the presence of amorphous GeO_2.

Crystal data

$In_{1.08}Gd_{0.92}Ge_2O_7$
$M_r = 525.90$
Monoclinic, $C2/m$
$a = 6.8713$ (4) Å
$b = 8.8805$ (5) Å
$c = 4.8976$ (3) Å
$\beta = 101.525$ (2)°
$V = 292.83$ (3) Å^3
$Z = 2$

$D_x = 5.964$ Mg m^{-3}
Cu *Kα* radiation
$T = 295$ K
Specimen shape: flat sheet
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
$2\theta_{\min} = 14.00$, $2\theta_{\max} = 90.00°$
Increment in $2\theta = 0.02°$

Refinement

$R_p = 0.118$
$R_{\rm exp} = 0.07$
$R_B = 0.026$
$S = 1.68$
Increment in $2\theta = 0.02°$
Wavelengths of incident radiation: 1.54056 and 1.544 Å
Excluded region(s): none

Profile function: pseudo-Voigt modified according to Thompson *et al.* (1987)
330 reflections
31 parameters
Weighting scheme based on measured s.u.'s
Orientation correction: none

The powder diffraction pattern was indexed using the *TREOR* program (Werner, 1985). Following the criteria employed by Cruickshank *et al.* (1962), we considered that the new title $InGdGe_2O_7$ compound crystallizes in the thortveitite structure, the symmetry of which is described by the space group *C2/m* (No. 12).

Table 1
Selected geometric parameters (Å, °).

Gd—O2^{i}	2.239 (6)	Ge—O1	1.703 (2)
Gd—O3	2.202 (6)	Ge—O2	1.698 (9)
Gd—O3^{ii}	2.316 (6)	Ge—O3	1.695 (6)
O1—Ge—O2	103.9 (6)	O2—Ge—O3	113.3 (2)
O1—Ge—O3	106.0 (4)	O3—Ge—O3^{iii}	113.5 (6)

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

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The Rietveld method was used to refine the crystal structure, using initial parameters from the $In_2Ge_2O_7$ thortveitite-type structure (ICDD card No. 26-768; structural data from Gaewdang *et al.*, 1994). A total of 31 independent parameters were refined: zero point, scale factor, six background polynomial coefficients, unit-cell parameters, half-width and asymmetry parameters for the peak shape, atomic coordinates, and isotropic atomic displacement parameters.

Data collection: *DIFFRAC/AT* (Siemens, 1993); cell refinement: *DICVOL*91 (Boultif & Louer, 1991); program(s) used to refine structure: *FULLPROF* (Wiles & Young, 1981); molecular graphics: *ATOMS* (Dowty, 1994); software used to prepare material for publication: *ATOMS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1375). Services for accessing these data are described at the back of the journal.

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