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## Structure Reports

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Rietveld refinement of  $Y_2GeO_5$ Eric M. Rivera-Muñoz<sup>a\*</sup> and Lauro Bucio<sup>b</sup>

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Key indicators: powder X-ray study;  $T = 300$  K; mean  $\sigma(Y-O) = 0.009$  Å;  $R$  factor = 0.053;  $wR$  factor = 0.069; data-to-parameter ratio = 5.5.

$Y_2GeO_5$  (yttrium germanium pentaoxide) was synthesized by solid-state reaction at 1443 K. The arrangement, which has monoclinic symmetry, is isostructural with  $Dy_2GeO_5$  and presents two independent sites for the Y atoms. Around these atoms there are distorted six-coordinated  $YO_6$  octahedra and seven-coordinated  $YO_7$  pentagonal bipyramids. The  $YO_7$  polyhedra are linked together, sharing their edges along a surface parallel to  $ab$ , forming a sheet. Each of these parallel sheets is interconnected by means of  $GeO_4$  tetrahedra, sharing an edge (or vertex) on one side and a vertex (or edge) on the other adjacent side. Parallel sheets of  $YO_7$  polyhedra are also interconnected by undulating chains of  $YO_6$  octahedra along the  $c$  axis. These octahedra are joined together, sharing a common edge, to form the chain and share edges with the  $YO_7$  polyhedra of the sheets.

## Related literature

For the isotypic structure of  $Dy_2GeO_5$ , see: Brixner *et al.* (1985). Different synthesis methods have been reported for this compound, including preparation by conventional r.f. magnetron sputtering (Minami *et al.*, 2003), solid-state reactions at high temperatures (Zhao *et al.*, 2003), MOCVD and LSMCD (Natori *et al.*, 2004). For bond-valence parameters, see: Brese & O'Keefe (1991), and for the bond-valence model, see: Brown (1981, 1992). For oxide phosphors, see: Minami *et al.* (2001, 2002, 2004). Data used to model the second phase present in the reaction product,  $Y_2Ge_2O_7$ , were taken from Redhammer *et al.* (2007). For related literature on technological applications, see: Fei *et al.* (2003).

## Experimental

## Crystal data

$Y_2GeO_5$	$c = 12.8795$ (2) Å
$M_r = 330.43$	$\beta = 101.750$ (3)°
Monoclinic, $I2/a$	$V = 901.66$ (3) Å <sup>3</sup>
$a = 10.4706$ (2) Å	$Z = 8$
$b = 6.8292$ (1) Å	Cu $K\alpha$ radiation

$T = 300$  K  
Specimen shape: flat sheet  
 $20 \times 20 \times 0.2$  mm

Specimen prepared at 1443 K  
Particle morphology: spherical,  
white

## Data collection

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

Scan method: step  
 $2\theta_{\min} = 8.0$ ,  $2\theta_{\max} = 80.0^\circ$   
Increment in  $2\theta = 0.02^\circ$

## Refinement

$R_p = 0.053$   
 $R_{wp} = 0.069$   
 $R_{exp} = 0.024$   
 $S = 2.90$   
Wavelength of incident radiation:  
1.540560 Å

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

Data collection: *DIFFRAC/AT* (Siemens, 1993); cell refinement: *DICVOL91* (Boultif & Louër 1991); data reduction: *FULLPROF* (Rodríguez-Carvajal, 2006); method used to solve structure: coordinates taken from an isotypic compound (Brixner *et al.*, 1985); program(s) used to refine structure: *FULLPROF*; molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *FULLPROF*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2110).

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## supporting information

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## Rietveld refinement of $Y_2GeO_5$

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### S1. Comment

Field emission display (FED) constitutes the next generation of information display devices. Its advantages include portable size with low power consumption, broad viewing angle, and wide operating-temperature range among others (Zhao *et al.*, 2003). New multicomponent oxide phosphor, Mn-activated  $Y_2O_3-GeO_2$ , is promising as the thin-film emitting layer for thin-film electroluminescent (TFEL) devices (Minami *et al.*, 2001). The oxide phosphor for use in those electroluminescent devices is formed from yttrium oxide and a transition metal as an activator, or from Y—Ge—O oxide and one metallic element to form  $M:Y_2GeO_5$  where  $M$  is a metal (Minami *et al.*, 2002; Minami *et al.*, 2004). Other reported use for  $Y_2GeO_5$  consists in piezoelectric ceramics in the form of films which include a complex oxide material having an oxygen octahedral structure and a paraelectric material having a catalytic effect for the complex oxide material in a mixed state. Paraelectric material could be a layered compound having an oxygen tetrahedral structure which includes one compound with the form  $MSiO_x$  ( $M$ =metal) and  $Y_2GeO_5$  (Natori *et al.*, 2004). Fig. 1a show a fragment of the crystal structure of  $Y_2GeO_5$  along the  $ab$  plane in which  $YO_7$  polyhedra share common edges forming a mesh. These  $YO_7$  polyhedra are represented as medium slate blue. Over the mesh, there are isolated  $GeO_4$  tetrahedra, which are represented in yellow in Fig. 1a. Each one of these parallel sheets are interconnected by means of  $GeO_4$  tetrahedra, sharing an edge (or vertex) in one side and a vertex (or edge) in the other adjacent side respectively as can be seen in Fig. 1b. Undulating chains of  $YO_6$  octahedra along the  $c$  axis are represented in gray in Fig. 1c in which the  $YO_7$  polyhedra were not represented in order to clarify this feature of the arrangement. The chains of  $YO_6$  octahedra also interconnect the parallel sheets of  $YO_7$  polyhedra, as can be seen in the unit cell of  $Y_2GeO_5$  represented in Fig. 1d. Bond valence calculations were made using the recommended bond-valence parameters for oxides published by Brese & O'Keeffe (1991). Bond valence sum (BVS) around six-coordinated Y1, seven-coordinated Y2, and Ge give the values of 3.03, 2.76 and 4.08 respectively, being the first and the last closer to the values of +3 and +4 expected for the yttrium and germanium atoms respectively. The second value of 2.76 was first interpreted as stretched bonds around Y2 exist, but this suggestion was withdrawn because there is no compressed cation in the unit cell capable to balance the supposed stretched bonds around Y2, as it is established in the Brown's bond valence model (Brown, 1981) for evaluating the existence of stresses in the crystal. In fact, calculating the so called *Global Instability Index*, which is obtained as the root mean square of the bond-valence sum deviation for all the  $N$  atoms present in the asymmetric unit (Brown, 1992) a value of 0.06 was obtained suggesting no strain. This is a remarkably low value for a Rietveld refinement (for a well refined and unstrained structure this is less than 0.1). Then, the low value of the bond valence sum around Y2 is well within normal limits for a Rietveld refinement where larger deviations are typically found.

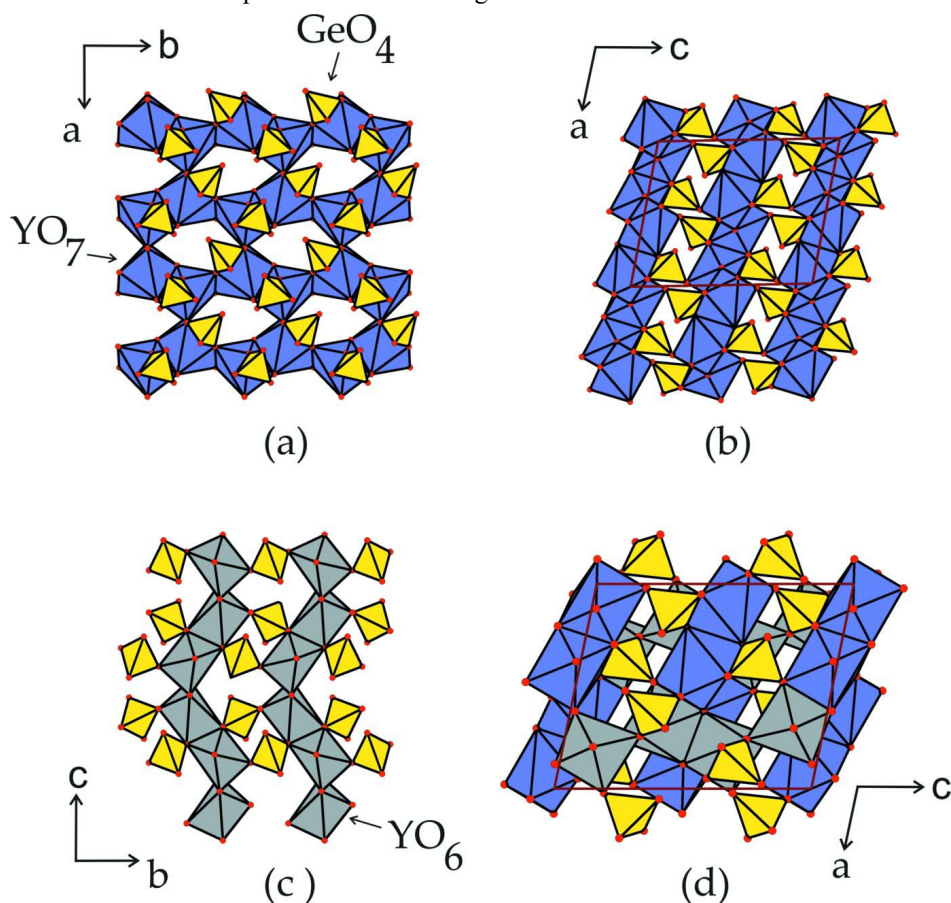
### S2. Experimental

The reactive mixture was prepared from  $Y_2O_3$  (Aldrich, 99.99%) and  $GeO_2$  (CERAC 99.999%) according to the stoichiometric proportions desired. The mixture was first powdered using an agate mortar; and then was heated in air in a

tube furnace at 1373 K for 5 days with intermediate regrindings. A second thermal treatment at 1443 K for two days was applied. The characterization of the bulk material by conventional X-ray powder diffraction data indicated the presence of a well crystallized phase showing reflections that match with the isostructural phase  $\text{DyGeO}_5$  (PDF 01-078-0478). Very small amount of a secondary phase  $\text{Y}_2\text{Ge}_2\text{O}_7$  (PDF 38-288) was identified.

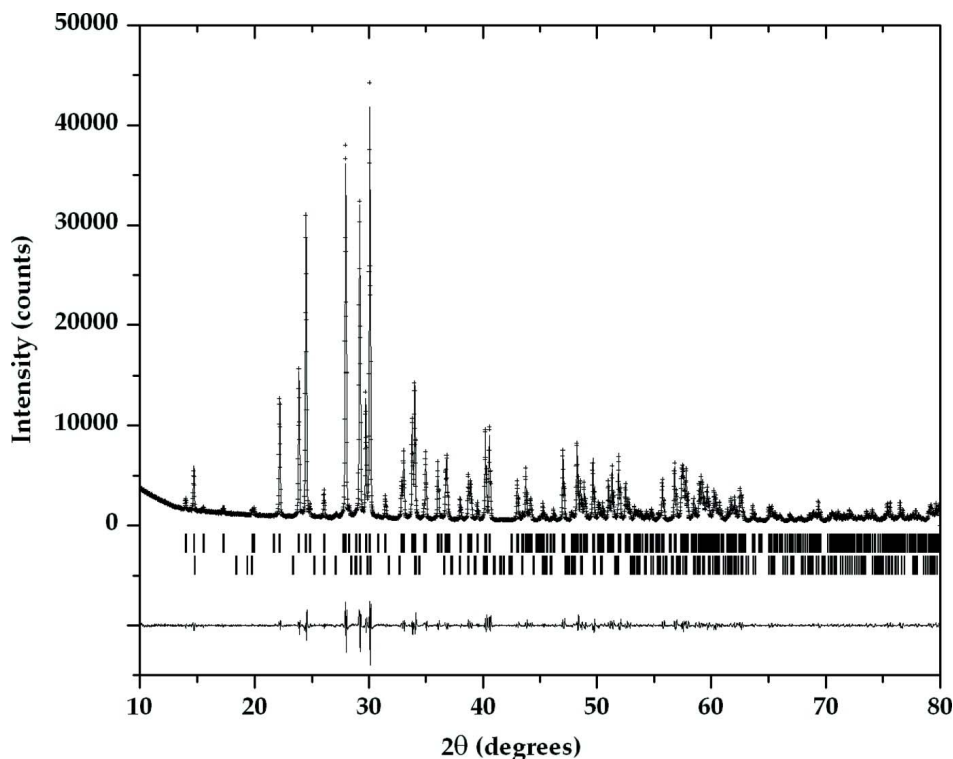
### S3. Refinement

The starting structural parameters for perform a Rietveld refinement of the  $\text{Y}_2\text{GeO}_5$  phase were taken from the isostructural data reported for  $\text{Dy}_2\text{GeO}_5$  (ICSD 61373) by Brixner *et al.* (1985). For modeling the second phase  $\text{Y}_2\text{Ge}_2\text{O}_7$  (ICSD 240989), the data were those reported by Redhammer *et al.* (2007). The following parameters were refined: zero point and scale factors, cell parameters, half-width profile parameters, overall temperature factors, atomic coordinates, and asymmetries. For the  $\text{Y}_2\text{Ge}_2\text{O}_7$  phase the atomic coordinates were fixed to their starting values. The final Rietveld refinement of conventional diffraction pattern is shown in Fig. 2.



**Figure 1**

(a) View of a  $\text{YO}_7$  layer in the  $\text{Y}_2\text{GeO}_5$  structure ( $ab$  projection).  $\text{YO}_7$  polyhedra are represented in medium slate blue while  $\text{GeO}_4$  tetrahedra are represented in yellow. (b) View of the  $\text{Y}_2\text{GeO}_5$  structure ( $ac$  projection). The layers formed by  $\text{YO}_7$  polyhedra are linked together by  $\text{GeO}_4$  tetrahedra. (c) Chains of  $\text{YO}_6$  octahedra (in gray) undulating along the  $c$  axis sharing common edges and linked with other chains by mean of  $\text{GeO}_4$  tetrahedra. (d) Unit cell for  $\text{Y}_2\text{GeO}_5$  structure.

**Figure 2**

Rietveld refinement for 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  $Y_2GeO_5$  (top) and  $Y_2Ge_2O_7$  (bottom) as secondary phase.

### yttrium germanium pentaoxide

#### Crystal data

$Y_2GeO_5$

$M_r = 330.43$

Monoclinic,  $I2/a$

Hall symbol:  $-I\ 2ya$

$a = 10.4706\ (2)\ \text{\AA}$

$b = 6.8292\ (1)\ \text{\AA}$

$c = 12.8795\ (2)\ \text{\AA}$

$\beta = 101.750\ (3)^\circ$

$V = 901.66\ (3)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1200$

$D_x = 4.868\ \text{Mg m}^{-3}$

Cu  $K\alpha$  radiation,  $\lambda = 1.540560\ \text{\AA}$

$T = 300\ \text{K}$

Particle morphology: spherical

white

flat sheet,  $20 \times 20\ \text{mm}$

Specimen preparation: Prepared at 1443 K

#### Data collection

Bruker Advance D8  
diffractometer

Radiation source: sealed X-ray tube, Cu  $K\alpha$

Graphite monochromator

Specimen mounting: packed powder sample  
container

Data collection mode: reflection

Scan method: step

$2\theta_{\min} = 7.979^\circ$ ,  $2\theta_{\max} = 80.002^\circ$ ,  $2\theta_{\text{step}} = 0.020^\circ$

Refinement

Least-squares matrix: full with fixed elements  
 per cycle  
 $R_p = 0.053$   
 $R_{wp} = 0.069$   
 $R_{exp} = 0.024$   
 $\chi^2 = 8.410$   
 3704 data points  
 Profile function: pseudo-Voigt modified by  
 Thompson *et al.* (1987)

105 parameters  
 Weighting scheme based on measured s.u.'s  
 $(\Delta/\sigma)_{max} = 0.02$   
 Background function: 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{iso}^*/U_{eq}$
Y1	0.3011 (2)	0.6277 (2)	0.6380 (1)	0.0096 (7)
Y2	0.0708 (2)	0.2567 (3)	0.5355 (1)	0.0090 (7)
Ge1	0.6236 (2)	0.5933 (3)	0.8155 (2)	0.0121 (9)
O1	0.1210 (9)	0.604 (1)	0.5178 (8)	0.009 (2)
O2	0.2950 (9)	0.298 (1)	0.6172 (7)	0.009 (2)
O3	0.5212 (9)	0.654 (1)	0.6971 (8)	0.009 (2)
O4	0.551 (1)	-0.006 (1)	0.4155 (8)	0.009 (2)
O5	0.2412 (8)	0.572 (1)	0.7926 (8)	0.009 (2)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Y1—O1	2.189 (8)	Y2—O2 <sup>i</sup>	2.655 (10)
Y1—O1 <sup>i</sup>	2.321 (10)	Y2—O3 <sup>iv</sup>	2.327 (10)
Y1—O2	2.270 (8)	Y2—O4 <sup>i</sup>	2.358 (9)
Y1—O3	2.283 (8)	Y2—O4 <sup>v</sup>	2.287 (9)
Y1—O5	2.238 (10)	Ge1—O2 <sup>vi</sup>	1.767 (8)
Y1—O5 <sup>ii</sup>	2.316 (8)	Ge1—O3	1.727 (8)
Y2—O1	2.447 (8)	Ge1—O4 <sup>vii</sup>	1.732 (10)
Y2—O1 <sup>iii</sup>	2.203 (8)	Ge1—O5 <sup>viii</sup>	1.739 (9)
Y2—O2	2.386 (8)		
Y1—O1—Y1 <sup>ix</sup>	53.6 (2)	Y1—O2—Y2 <sup>xiii</sup>	118.8 (3)
Y1—O1—Y2 <sup>x</sup>	128.7 (3)	Y2 <sup>xii</sup> —O2—Y2 <sup>xiii</sup>	61.19 (6)
Y1 <sup>ix</sup> —O1—Y2 <sup>x</sup>	78.64 (6)	Y1—O3—Y2 <sup>xiv</sup>	110.7 (3)
Y1 <sup>ix</sup> —O1—Y2 <sup>xi</sup>	90.44 (7)	Y2 <sup>xv</sup> —O4—Y2 <sup>xvi</sup>	124.20 (7)
Y2 <sup>x</sup> —O1—Y2 <sup>xi</sup>	157.05 (6)	Y1—O5—Y1 <sup>xvii</sup>	89.8 (2)
Y1—O2—Y2 <sup>xii</sup>	97.4 (2)		

Symmetry codes: (i)  $-x+1/2, y, -z+1$ ; (ii)  $-x+1/2, -y+3/2, -z+3/2$ ; (iii)  $-x, -y+1, -z+1$ ; (iv)  $x-1/2, -y+1, z$ ; (v)  $x-1/2, -y, z$ ; (vi)  $-x+1, y+1/2, -z+3/2$ ; (vii)  $x, -y+1/2, z+1/2$ ; (viii)  $x+1/2, -y+1, z$ ; (ix)  $-x+3/2, y, -z+1$ ; (x)  $-x, -y, -z$ ; (xi)  $x+1/2, -y+1, z+1$ ; (xii)  $-x+1/2, y, -z$ ; (xiii)  $-x+1, -y, -z+1$ ; (xiv)  $-x+3/2, y+1, -z$ ; (xv)  $x+1, y, z+1$ ; (xvi)  $-x+3/2, y, -z$ ; (xvii)  $-x+3/2, y+2, -z+2$ .