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Rubidium gadolinium bis(tungstate)

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The structure of rubidium gadolinium bis(tungstate), $RbGd(WO_4)_2$, has been determined. The crystal is built up from corner- and edge-sharing WO_6 octahedral and GdO_8 polyhedral groups, giving rise to a Gd–WO_4 polyhedral backbone surrounding structural cavities filled with Rb^+ cations. The Gd and Rb atoms lie on twofold axes.

Comment

Monoclinic double tungstate single crystals, with the formula $KRE(WO_4)_2$ (KGW), RE being the rare earths, are currently receiving attention as hosts for self-induced frequency shifting (Kaminskii *et al.*, 1998). The low-temperature phase of potassium gadolinium tungstate, $KGd(WO_4)_2$, is a promising laser material and has been extensively studied (Kushawaha *et al.*, 1993). In this paper, we present the synthesis and structural determination of the new rubidium gadolinium bis(tungstate), $RbGd(WO_4)_2$ (RGW), refined from single-crystal data. The structure is a three-dimensional network of WO_6 octahedra and GdO_8 square-antiprism polyhedra sharing edges and corners. Fig. 1 shows the framework of the RGW crystal projected along the [101] direction.

The WO_6 octahedra are distorted, with each coordinating W cation displaced by 0.36 Å from the mean of its six O vertices. This displacement 'dipole' is orientated along a pseudo-threefold axis of the octahedra, with inversion-related octahedral pairs joined by a common $O1\cdots O1^{i}$ edge [2.405 Å; symmetry code: (i) $-x, -y+1, -z$]. The inversion symmetry centre at the shared-edge mid-point is strongly suggestive of antiferroelectric properties. The W—O bonds span the range 1.768 (9)–2.325 (1) Å, with a mean distance of 1.959 (7) Å. Pairs of distorted octahedral units form a double chain along the crystallographic *c* axis and are connected by sharing common O3 vertices. The shortest $W1\cdots W1^{i}$ distance is 3.265 (0) Å, across the shared edge of the edge-sharing octahedra. Between the corner-sharing octahedra, the distance between W atoms is significantly larger, at 3.80 (3) Å [$W1\cdots W1^{viii}$; symmetry code: (viii) $x, -y+1, z+\frac{1}{2}$]. These values are almost in the same range as those found in $KGd(WO_4)_2$ and $KYb(WO_4)_2$ (Pujol *et al.*, 2001)

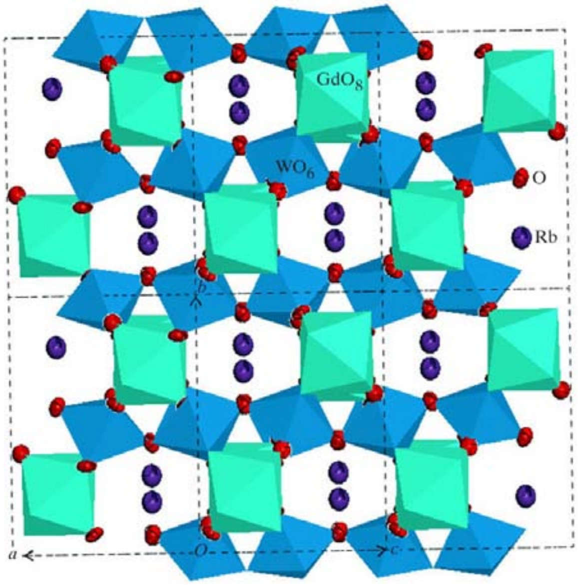

Figure 1
A projection of the RGW structure along the [101] direction. Displacement ellipsoids are drawn at the 50% probability level.

The Gd sites are eight-coordinated, with four pairs of Gd—O distances ranging from 2.310 (1) to 2.707 (9) Å, and arranged as a square antiprism. These polyhedra form a single chain along the [101] direction by alternately sharing $O2–O4^{ix}$ edges [3.039 Å; symmetry code: (ix) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$] and $O2^{iv}\cdots O2^{x}$ edges [3.028 Å; symmetry codes: (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (x) $-x, y, -z+\frac{1}{2}$]. The $Gd\cdots Gd1^{xi}$ distance within a chain is 4.049 Å [symmetry code: (xi) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$], while between chains the $Gd1\cdots Gd1^{i}$ distance is 6.7 Å. The shared edge between WO_6 octahedra ($O1\cdots O1^{i}$ = 2.405 Å) is the shortest in the structure and, likewise, the second-shortest edge [$O1^{vii}\cdots O2$ = 2.519 Å; symmetry code: (vii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$] is one that is shared between the tungstate and gadolinium polyhedra.

The Rb^+ cation is 12-coordinated by O atoms, forming a distorted icosahedron. These polyhedra form a bidimensional layer consisting of chains, which share edges in the [101] and [$\overline{1}$10] directions. These chains fill the holes in the framework of gadolinium and tungstate polyhedra. All the polyhedra contributing to the monoclinic RGW structure are strongly connected by shared edges and vertices.

Experimental

$GdRb(WO_4)_2$ single crystals were grown by the top-seeded solution growth (TSSG) slow-cooling technique, using $Rb_2W_2O_7$ as solvent. A solution composition of 20 mol% of solute and 80% of solvent was chosen. The solutions used in the crystal growth experiments, weighing about 200 g, were prepared in a cylindrical Pt crucible (60 mm in diameter) by melting and decomposing the appropriate quantities of Gd_2O_3, Rb_2O_3 and WO_3. Homogenization of the solutions was achieved by maintaining them at about 323 K above the

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expected saturation temperature for 24 h. After homogenization of the solution, a Pt disc (diameter 11 mm) rotating at 30 r.p.m. was added. The solution temperature was then decreased at a rate of 0.1 K h^{-1} until crystals nucleated on the disc, and then at a rate of 1–1.5 K h^{-1}. Crystals of RGW were removed after the sample had reached room temperature.

Crystal data

$RbGd(WO_4)_2$
$M_r = 738.42$
Monoclinic, $C2/c$
$a = 10.6953$ (12) Å
$b = 10.5017$ (11) Å
$c = 7.6064$ (11) Å
$\beta = 130.504$ (7)°
$V = 649.61$ (14) $Å^3$
$Z = 4$

$D_x = 7.550$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 33 reflections
$\theta = 5.0$–15.0°
$\mu = 52.87$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.20 × 0.18 × 0.13 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
$T_{min} = 0.013$, $T_{max} = 0.045$
1197 measured reflections
951 independent reflections
848 reflections with $I > 2\sigma(I)$

$R_{int} = 0.085$
$\theta_{max} = 30.0°$
$h = -1 \rightarrow 15$
$k = -14 \rightarrow 1$
$l = -10 \rightarrow 8$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.136$
$S = 1.11$
951 reflections
57 parameters
$w = 1/[\sigma^2(F_o^2) + (0.089P)^2 + 31.6366P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 5.38$ e $Å^{-3}$
$\Delta\rho_{min} = -6.38$ e $Å^{-3}$
Extinction correction: *SHELXTL* (Bruker, 1997)
Extinction coefficient: 0.0070 (5)

Table 1
Selected geometric parameters (Å).

W1—O4	1.768 (9)	Gd1—O2^{iv}	2.384 (9)
W1—O3	1.776 (10)	Gd1—O2	2.707 (9)
W1—O2	1.832 (9)	Rb1—O3	2.853 (10)
W1—O1	1.970 (10)	Rb1—O3^{vi}	2.880 (10)
W1—O1^{i}	2.084 (9)	Rb1—O4^{v}	2.975 (10)
W1—O3^{ii}	2.325 (10)	Rb1—O1	3.070 (10)
Gd1—O1^{i}	2.310 (10)	Rb1—O2^{vii}	3.130 (10)
Gd1—O4^{iii}	2.335 (9)	Rb1—O4^{vii}	3.359 (10)

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

A numerical or analytical absorption correction should be used for the intensity data, because the product of the linear absorption coefficient (μ) and the median crystal dimension is greater than 3.0, but there were no regular faces of the crystal for that approach. Therefore, a ψ-scan absorption correction was attempted. After the correction, the structure was solved easily. The positions of three heavy atoms were obtained correctly from the Patterson map and four O atoms from Fourier syntheses. All atoms were refined with anisotropic displacement parameters. The value of the maximum residual electron density in the final difference Fourier map is less than 0.1 of the heaviest atomic number and the value of the minimum is larger than −0.1 of that. The peak and hole are 0.79 and 0.74 Å, respectively, from the W atom.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1053). Services for accessing these data are described at the back of the journal.

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