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Crystal structure of defect scheelite-type $Nd_{2/3}[WO_4]$

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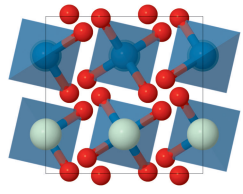
Neodymium(III) *ortho*-oxidotungstate(VI) was synthesized as a side-product in an unsuccessful synthesis attempt at fluoride derivatives of neodymium tungstate in fused silica ampoules, using neodymium(III) oxide, neodymium(III) fluoride and tungsten trioxide. Violet, platelet-shaped single crystals of the title compound emerged of the bulk, which crystallize in the defect scheelite type with a trigonal dodecahedral coordination of oxide anions around the Nd^{3+} cations and the hexavalent tungsten cations situated in the centers of oxide tetrahedra.

3D view



Structure description

$Nd_{2/3}[WO_4]$ crystallizes in the defect scheelite structure type (space group $I4_1/a$, Dickinson, 1920; see Fig. 1). The tungsten cations (Wyckoff position 4*a*, site symmetry $\overline{4}$) form regular tetrahedra $[WO_4]^{2-}$ together with four oxide anions, exhibiting a bond length of 1.783 (4) Å. The neodymium cations (Wyckoff position 4*b*, site symmetry $\overline{4}$) are coordinated by eight oxide anions, forming a slightly distorted trigonal dodecahedron, in which two different bond lengths, 2.483 (4) Å and 2.516 (4) Å, each one appearing four times, are found (Fig. 2). The distance between two neodymium cations is 3.9116 (2) Å. The corresponding oxidomolybdate(IV), $Nd_{2/3}[MoO_4]$, crystallizes in the same structure type (Schustereit *et al.*, 2011).

Another, formula-analogous polymorph of neodymium(III) *ortho*-oxidotungstate(VI) with the composition $Nd_2[WO_4]_3$ is already known in literature (Weil *et al.*, 2009), with this compound crystallizing in the *scheelite*-derived $Eu_2[WO_4]_3$ structure type (space group *C*2/*c*; Templeton & Zalkin, 1963). The main difference between these polymorphs is the emergence of a fifth, slightly longer distance from W^{6+} to O^{2-} in $Nd_2[WO_4]_3$, resulting in $[W_2O_8]^{4-}$ entities, built of two edge-sharing rectangular pyramids being present in its crystal structure, while in the title compound $Nd_{2/3}[WO_4]$ the $[WO_4]^{2-}$ tetrahedra remain isolated from each other. A rare-earth metal oxidotungstate(VI),

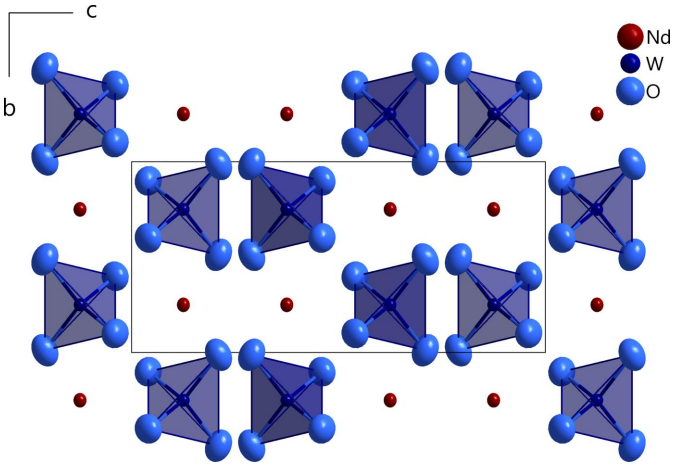


Figure 1
Augmented unit cell of $Nd_{2/3}[WO_4]$ in a view along [100], with $[WO_4]^{2-}$ anions in polyhedral representation and displacement ellipsoids drawn at the 95% probability level.

crystallizing in the scheelite-type with a fully occupied cationic position is known with Eu^{2+} cations, namely $Eu[WO_4]$ (López-Moreno *et al.*, 2011).

Synthesis and crystallization

Single-crystals of $Nd_{2/3}[WO_4]$ formed in an unsuccessful synthesis attempt to achieve fluoride derivatives of neodymium tungstate, which was performed in fused silica ampoules, utilizing neodymium trifluoride, neodymium(III) oxide and tungsten trioxide as starting materials at approximately 1123 K. The crystals emerged as violet platelets and remained stable under atmospheric conditions.

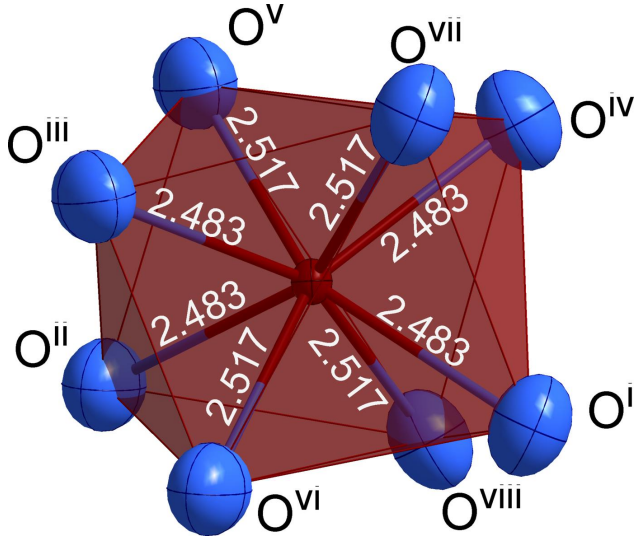


Figure 2
Cationic coordination sphere around the Nd^{3+} cation in the shape of a trigonal $[NdO_8]^{13-}$ dodecahedron; displacement ellipsoids are drawn at the 95% probability level. [Symmetry codes: (i) $y-\frac{1}{4}, -x+\frac{3}{4}, z+\frac{3}{4}$; (ii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-y+\frac{1}{4}, x-\frac{1}{4}, z+\frac{3}{4}$; (v) $x-\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$; (vi) $-x+\frac{1}{2}, -y+1, z+\frac{1}{2}$; (vii) $-y+\frac{3}{4}, x-\frac{1}{4}, -z+\frac{3}{4}$; (viii) $y-\frac{3}{4}, -x+\frac{3}{4}, -z+\frac{3}{4}$].

Table 1
Experimental details.

Crystal data	
Chemical formula	$Nd_{2/3}[WO_4]$
M_r	344.01
Crystal system, space group	Tetragonal, $I4_1/a$
Temperature (K)	293
a, c (Å)	5.3048 (3), 11.4999 (9)
V (Å^3)	323.62 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	45.98
Crystal size (mm)	0.09 × 0.08 × 0.06
Data collection	
Diffractometer	Stoe *IPDS*
Absorption correction	Numerical [*X-SHAPE* (Stoe & Cie, 1997); *HABITUS* (Herrendorf, 1995)]
T_{min}, T_{max}	0.015, 0.060
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2201, 291, 231
R_{int}	0.061
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.754
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.050, 1.01
No. of reflections	291
No. of parameters	15
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.08, −1.26

Computer programs: *DIF4* and *REDU4* (Stoe & Cie, 1991), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2005) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The site occupancy of the neodymium cations was fixed at 2/3 to maintain electroneutrality.

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References

Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Dickinson, R. G. (1920). *J. Am. Chem. Soc.* **42**, 85–93.
Herrendorf, W. (1995). *HABITUS*. Universities of Karlsruhe and Giessen, Germany.
López-Moreno, S., Rodríguez-Hernández, P., Muñoz, A., Romero, A. H. & Errandonea, D. (2011). *Phys. Rev. B*, **84**, 064108.
Schustereit, T., Müller, S. L., Schleid, T. & Hartenbach, I. (2011). *Crystals*, **1**, 244–253.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Stoe & Cie. (1991). *DIF4* and *REDU4*. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie. (1997). *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
Templeton, D. H. & Zalkin, A. (1963). *Acta Cryst.* **16**, 762–766.
Weil, M., Stöger, B. & Aleksandrov, L. (2009). *Acta Cryst.* E**65**, i45.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2024). **9**, x240175 [https://doi.org/10.1107/S2414314624001755]

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Neodymium(III) *ortho*-oxidotungstate(VI)

Crystal data

$Nd_{0.67}[WO_4]$
M_r = 344.01
Tetragonal, $I4_1/a$
a = 5.3048 (3) Å
c = 11.4999 (9) Å
V = 323.62 (4) Å^3
Z = 4
$F(000)$ = 584
D_x = 7.061 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1393 reflections
θ = 2.9–33.0°
μ = 45.98 mm^{-1}
T = 293 K
Platelet, violet
0.09 × 0.08 × 0.06 mm

Data collection

Stoe IPDS diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω–scans
Absorption correction: numerical [X-SHAPE (Stoe & Cie, 1997); HABITUS (Herrendorf, 1995)]
T_{min} = 0.015, T_{max} = 0.060
2201 measured reflections
291 independent reflections
231 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 32.4°, θ_{min} = 4.2°
h = −8→7
k = −8→7
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.050
S = 1.01
291 reflections
15 parameters
0 restraints
$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.08 e Å^{-3}
$\Delta\rho_{min}$ = −1.26 e Å^{-3}
Extinction correction: SHELXL (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.088 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Nd	0.000000	0.250000	0.625000	0.0163 (2)	0.6667
W	0.000000	0.250000	0.125000	0.0135 (2)	
O	0.2382 (8)	0.3998 (7)	0.0401 (3)	0.0221 (8)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nd	0.0176 (3)	0.0176 (3)	0.0139 (4)	0.000	0.000	0.000
W	0.0138 (2)	0.0138 (2)	0.0130 (3)	0.000	0.000	0.000
O	0.026 (2)	0.022 (2)	0.0185 (17)	0.0001 (15)	0.0047 (16)	0.0011 (16)

Geometric parameters (Å, º)

Nd—O^{i}	2.483 (4)	Nd—Nd^{ix}	3.9116 (2)
Nd—O^{ii}	2.483 (4)	Nd—Nd^{x}	3.9116 (2)
Nd—O^{iii}	2.483 (4)	Nd—Nd^{xi}	3.9116 (2)
Nd—O^{iv}	2.483 (4)	Nd—Nd^{xii}	3.9116 (2)
Nd—O^{v}	2.516 (4)	W—O^{xiii}	1.783 (4)
Nd—O^{vi}	2.516 (4)	W—O^{xiv}	1.783 (4)
Nd—O^{vii}	2.516 (4)	W—O^{xv}	1.783 (4)
Nd—O^{viii}	2.516 (4)	W—O	1.783 (4)
O^{i}—Nd—O^{ii}	125.78 (12)	O^{v}—Nd—O^{vii}	98.65 (6)
O^{i}—Nd—O^{iii}	125.78 (12)	O^{vi}—Nd—O^{vii}	98.65 (7)
O^{ii}—Nd—O^{iii}	80.25 (19)	O^{i}—Nd—O^{viii}	68.34 (10)
O^{i}—Nd—O^{iv}	80.2 (2)	O^{ii}—Nd—O^{viii}	72.96 (8)
O^{ii}—Nd—O^{iv}	125.78 (12)	O^{iii}—Nd—O^{viii}	152.39 (16)
O^{iii}—Nd—O^{iv}	125.78 (12)	O^{iv}—Nd—O^{viii}	77.05 (15)
O^{i}—Nd—O^{v}	152.39 (16)	O^{v}—Nd—O^{viii}	98.65 (7)
O^{ii}—Nd—O^{v}	68.34 (10)	O^{vi}—Nd—O^{viii}	98.65 (6)
O^{iii}—Nd—O^{v}	77.05 (15)	O^{vii}—Nd—O^{viii}	134.35 (18)
O^{iv}—Nd—O^{v}	72.96 (8)	O^{xiii}—W—O^{xiv}	107.43 (13)
O^{i}—Nd—O^{vi}	72.96 (8)	O^{xiii}—W—O^{xv}	107.43 (13)
O^{ii}—Nd—O^{vi}	77.05 (15)	O^{xiv}—W—O^{xv}	113.6 (3)
O^{iii}—Nd—O^{vi}	68.34 (10)	O^{xiii}—W—O	113.6 (3)
O^{iv}—Nd—O^{vi}	152.39 (16)	O^{xiv}—W—O	107.43 (13)
O^{v}—Nd—O^{vi}	134.35 (18)	O^{xv}—W—O	107.43 (13)
O^{i}—Nd—O^{vii}	77.05 (15)	W—O—Nd^{iii}	132.2 (2)
O^{ii}—Nd—O^{vii}	152.39 (16)	W—O—Nd^{xvi}	120.51 (19)
O^{iii}—Nd—O^{vii}	72.96 (8)	Nd^{iii}—O—Nd^{xvi}	102.95 (15)
O^{iv}—Nd—O^{vii}	68.34 (10)		

Symmetry codes: (i) *y*−1/4, −*x*+3/4, *z*+3/4; (ii) *x*−1/2, *y*, −*z*+1/2; (iii) −*x*+1/2, −*y*+1/2, −*z*+1/2; (iv) −*y*+1/4, *x*−1/4, *z*+3/4; (v) *x*−1/2, *y*−1/2, *z*+1/2; (vi) −*x*+1/2, −*y*+1, *z*+1/2; (vii) −*y*+3/4, *x*−1/4, −*z*+3/4; (viii) *y*−3/4, −*x*+3/4, −*z*+3/4; (ix) −*x*, −*y*, −*z*+1; (x) −*x*+1/2, −*y*+1/2, −*z*+3/2; (xi) −*x*−1/2, −*y*+1/2, −*z*+3/2; (xii) −*x*, −*y*+1, −*z*+1; (xiii) −*x*, −*y*+1/2, *z*; (xiv) −*y*+1/4, *x*+1/4, −*z*+1/4; (xv) *y*−1/4, −*x*+1/4, −*z*+1/4; (xvi) *x*+1/2, *y*+1/2, *z*−1/2.