

supplementary materials

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Scheelite-type NaDy(WO₄)₂

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Comment

In the past years an increasing interest in the synthesis and characterization of rare-earth double tungstate(VI) crystals with general formula $ARE(WO_4)_2$ (A = alkali metal, RE = rare-earth metal) has been observed due to their interesting magnetic, electric and optical properties (Perets *et al.*, 2007; Huang *et al.*, 2006; Li *et al.*, 1990; Han *et al.*, 2002). These compounds are attractive solid-state laser host materials because of their large rare-earth ion admittance. Most of these crystals have tetragonal symmetry and crystallize with the scheelite structure (CaWO₄) in space group $I4_1/a$ (Sillen & Nylander, 1943). In the title structure, the Ca²⁺ position of the original CaWO₄ structure is statistically occupied by Na⁺ and Dy³⁺ ions in an 1:1 ratio. The crystal structure of NaDy(WO₄)₂ is composed of a two-direction packing of isolated WO₄ tetrahedra interconnected by distorted [(Na/Dy)O₈] dodecahedra, as shown in Fig. 2.

Experimental

Single crystal of NaDy(WO₄)₂ were prepared by a high temperature solution reaction, using analytical reagents of Dy₂O₃, Na₂CO₃ and WO₃ in the molar ratio of Na: Dy: W = 8:1:10. The starting mixture was finely ground in an agate mortar to ensure the best homogeneity and reactivity, and then transferred to a platinum crucible to be heated at a temperature of 773 K for 8 h. The sintered product was reground and continuously heated at 1273 K for 20 h, cooled to 673 K at a rate of 4 K/h, and then quenched to room temperature. A few light yellow and prismatically shaped crystals of the title compound were obtained.

Refinement

The Na1 and Dy1 atoms are in a substitutional-type disorder in the structure. Therefore the atomic position and anisotropic displacement parameters of Na1 and Dy1 atoms were constrained to be identical. In the initial least-squares refinement, the occupancy factors of Na1 and Dy1 atoms were set to be free. The results show that the occupancy factors were close to 1:1, *viz* Na1: Dy1 = 0.50273: 0.49727, and were eventually fixed in a 1:1 ratio. The highest peak in the final difference electron density map is 1.55 e/Å³ from the W1 site, and the deepest hole is -1.40 e/Å³ from the Na1/Dy1 site.

Figures

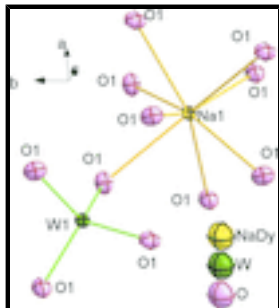


Fig. 1. Part of the structure of $\text{NaDy}(\text{WO}_4)_2$ showing the labelling of the atoms (displacement ellipsoids are drawn at the 50% probability level).

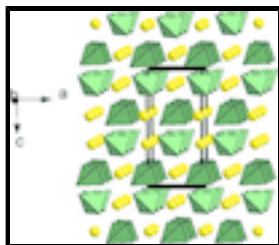


Fig. 2. View of the crystal structure of $\text{NaDy}(\text{WO}_4)_2$ (WO_4 tetrahedra are shaded in sea-green; Na/Dy atoms are drawn as yellow balls).

Sodium dysprosium(III) bis[tungstate(VI)]

Crystal data

$\text{NaDy}(\text{WO}_4)_2$

$M_r = 681.19$

Tetragonal, $I4_1/a$

Hall symbol: $-I\ 4ad$

$a = 5.2545\ (5)\ \text{\AA}$

$c = 11.4029\ (15)\ \text{\AA}$

$V = 314.83\ (6)\ \text{\AA}^3$

$Z = 2$

$F(000) = 578$

$D_x = 7.186\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 405 reflections

$\theta = 3.6\text{--}27.5^\circ$

$\mu = 48.27\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Prism, light yellow

$0.10 \times 0.10 \times 0.08\ \text{mm}$

Data collection

Rigaku Mercury70
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: $14.6306\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 1997)

$T_{\min} = 0.263$, $T_{\max} = 1.000$

1128 measured reflections

181 independent reflections

143 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 4.3^\circ$

$h = -6 \rightarrow 6$

$k = -6 \rightarrow 6$

$l = -14 \rightarrow 13$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.024$	$w = 1/[\sigma^2(F_o^2) + (0.0045P)^2]$
$wR(F^2) = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.87$	$(\Delta/\sigma)_{\max} < 0.001$
181 reflections	$\Delta\rho_{\max} = 1.55 \text{ e } \text{\AA}^{-3}$
15 parameters	$\Delta\rho_{\min} = -1.40 \text{ e } \text{\AA}^{-3}$
0 restraints	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.0295 (17)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Na1	0.5000	-0.2500	0.1250	0.0068 (4)	0.50
Dy1	0.5000	-0.2500	0.1250	0.0068 (4)	0.50
W1	0.0000	0.2500	0.1250	0.0091 (4)	
O1	0.2419 (14)	0.0977 (13)	0.0404 (6)	0.0187 (16)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.0090 (6)	0.0090 (6)	0.0024 (8)	0.000	0.000	0.000
Dy1	0.0090 (6)	0.0090 (6)	0.0024 (8)	0.000	0.000	0.000
W1	0.0098 (4)	0.0098 (4)	0.0076 (6)	0.000	0.000	0.000
O1	0.024 (5)	0.017 (4)	0.015 (3)	0.001 (3)	0.003 (3)	0.001 (3)

Geometric parameters (\AA , $^\circ$)

(Na/Dy)1—O1 ⁱ	2.457 (7)	(Na/Dy)1—O1 ^{vii}	2.471 (7)
(Na/Dy)1—O1 ⁱⁱ	2.457 (7)	(Na/Dy)1—O1	2.471 (7)

supplementary materials

(Na/Dy)1—O1 ⁱⁱⁱ	2.457 (7)	W1—O1 ^{viii}	1.785 (7)
(Na/Dy)1—O1 ^{iv}	2.457 (7)	W1—O1 ^{ix}	1.785 (7)
(Na/Dy)1—O1 ^v	2.471 (7)	W1—O1	1.785 (7)
(Na/Dy)1—O1 ^{vi}	2.471 (7)	W1—O1 ^x	1.785 (7)
O1 ⁱ —(Na/Dy)1—O1 ⁱⁱ	79.7 (3)	O1 ^{vi} —(Na/Dy)1—O1 ^{vii}	98.76 (12)
O1 ⁱ —(Na/Dy)1—O1 ⁱⁱⁱ	126.1 (2)	O1 ⁱ —(Na/Dy)1—O1	68.80 (16)
O1 ⁱⁱ —(Na/Dy)1—O1 ⁱⁱⁱ	126.1 (2)	O1 ⁱⁱ —(Na/Dy)1—O1	76.3 (3)
O1 ⁱ —(Na/Dy)1—O1 ^{iv}	126.1 (2)	O1 ⁱⁱⁱ —(Na/Dy)1—O1	73.31 (14)
O1 ⁱⁱ —(Na/Dy)1—O1 ^{iv}	126.1 (2)	O1 ^{iv} —(Na/Dy)1—O1	152.4 (3)
O1 ⁱⁱⁱ —(Na/Dy)1—O1 ^{iv}	79.7 (3)	O1 ^v —(Na/Dy)1—O1	98.76 (12)
O1 ⁱ —(Na/Dy)1—O1 ^v	152.4 (3)	O1 ^{vi} —(Na/Dy)1—O1	98.76 (12)
O1 ⁱⁱ —(Na/Dy)1—O1 ^v	73.31 (14)	O1 ^{vii} —(Na/Dy)1—O1	134.1 (3)
O1 ⁱⁱⁱ —(Na/Dy)1—O1 ^v	68.80 (16)	O1 ^{viii} —W1—O1 ^{ix}	107.0 (2)
O1 ^{iv} —(Na/Dy)1—O1 ^v	76.3 (3)	O1 ^{viii} —W1—O1	114.6 (4)
O1 ⁱ —(Na/Dy)1—O1 ^{vi}	73.31 (14)	O1 ^{ix} —W1—O1	107.0 (2)
O1 ⁱⁱ —(Na/Dy)1—O1 ^{vi}	152.4 (3)	O1 ^{viii} —W1—O1 ^x	107.0 (2)
O1 ⁱⁱⁱ —(Na/Dy)1—O1 ^{vi}	76.3 (3)	O1 ^{ix} —W1—O1 ^x	114.6 (4)
O1 ^{iv} —(Na/Dy)1—O1 ^{vi}	68.80 (16)	O1—W1—O1 ^x	107.0 (2)
O1 ^v —(Na/Dy)1—O1 ^{vi}	134.1 (3)	W1—O1—Dy1 ⁱⁱ	131.4 (3)
O1 ⁱ —(Na/Dy)1—O1 ^{vii}	76.3 (3)	W1—O1—(Na/Dy)1 ⁱⁱ	131.4 (3)
O1 ⁱⁱ —(Na/Dy)1—O1 ^{vii}	68.80 (16)	W1—O1—(Na/Dy)1	120.8 (3)
O1 ⁱⁱⁱ —(Na/Dy)1—O1 ^{vii}	152.4 (3)	Dy1 ⁱⁱ —O1—(Na/Dy)1	103.7 (3)
O1 ^{iv} —(Na/Dy)1—O1 ^{vii}	73.31 (14)	(Na/Dy)1 ⁱⁱ —O1—(Na/Dy)1	103.7 (3)
O1 ^v —(Na/Dy)1—O1 ^{vii}	98.76 (12)		

Symmetry codes: (i) $x, y-1/2, -z$; (ii) $-x+1, -y, -z$; (iii) $y+1/4, -x+1/4, z+1/4$; (iv) $-y+3/4, x-3/4, z+1/4$; (v) $y+3/4, -x+1/4, -z+1/4$; (vi) $-y+1/4, x-3/4, -z+1/4$; (vii) $-x+1, -y-1/2, z$; (viii) $-x, -y+1/2, z$; (ix) $-y+1/4, x+1/4, -z+1/4$; (x) $y-1/4, -x+1/4, -z+1/4$.

Fig. 1

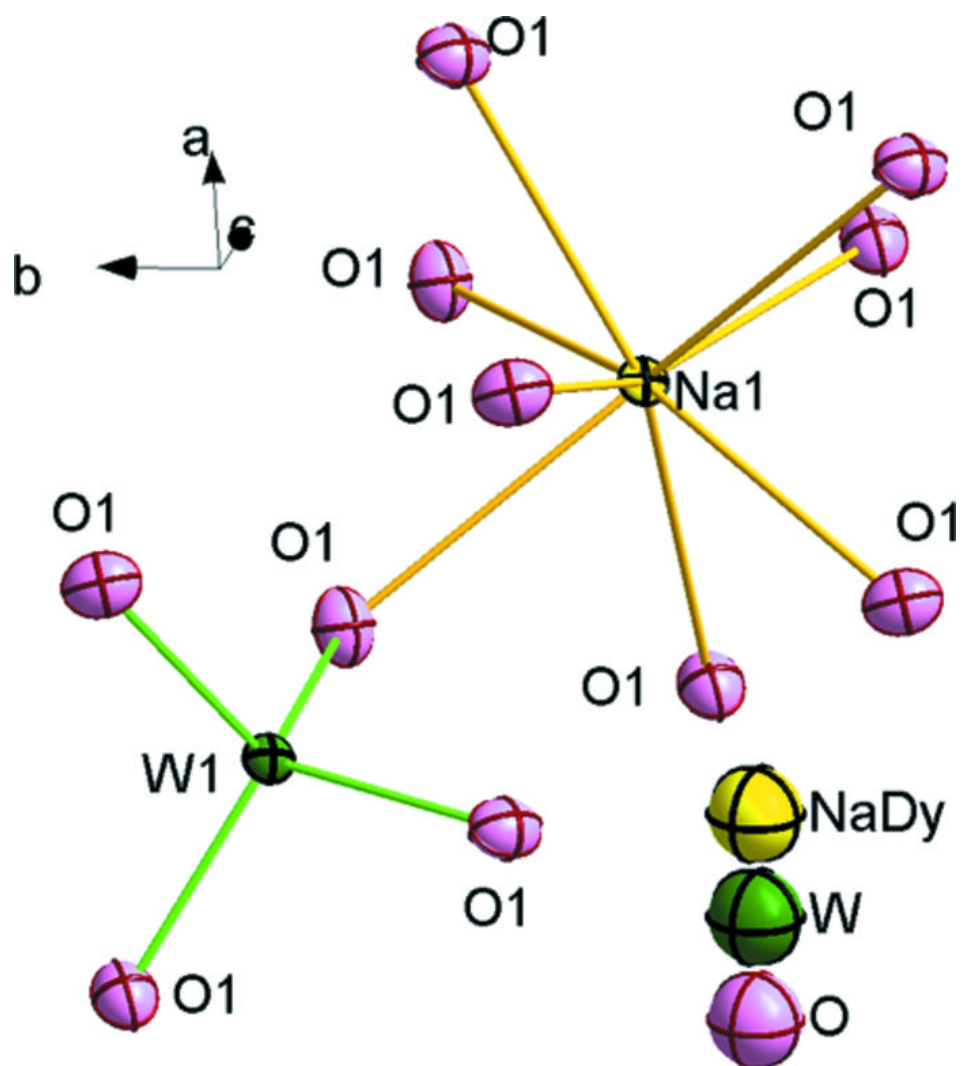


Fig. 2

