Crystal structure of pentacalcium [tetranitridotungstate(VI)] dioxide, $Ca_5[WN_4]O_2$

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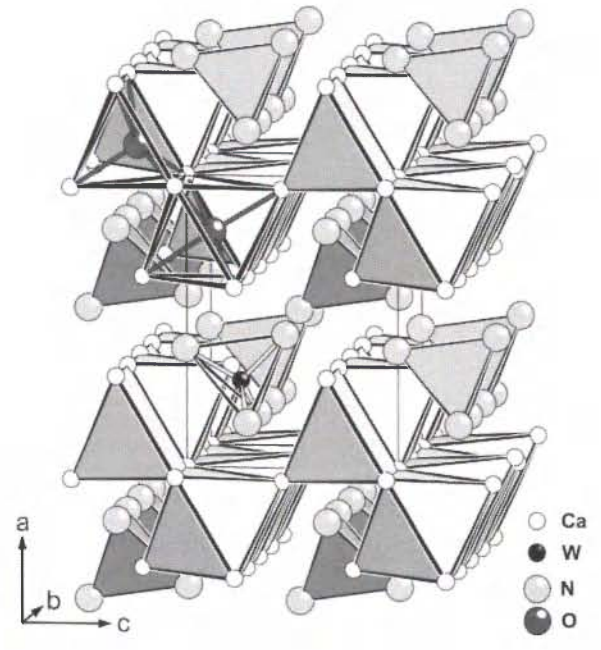

Abstract

$Ca_5N_4O_2W$, monoclinic, $P12_1/m1$ (No. 11), $a = 6.153(1)$ Å, $b = 6.795(1)$ Å, $c = 8.506(1)$ Å, $\beta = 90.39(1)°$, $V = 355.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.021$, $wR_{ref}(F^2) = 0.052$, $T = 293$ K.

Source of material

Yellow single crystals were obtained by reaction of pellets of Ca_3N_2, CaO and W (molar ratio 4:2:1). The reaction was carried out under N_2 at ambient pressure in W crucibles. The mixtures were heated to 1223 K (100 K/h). After a period of 36 h the products were cooled down (50 K/h) to ambient temperature. Starting materials and products are sensitive to moisture and air.

Discussion

Only few crystal structures of alkaline earth nitridometalate oxides of molybdenum and tungsten are known up to now: $(Li_2Ca_4O)_3[MoN_4]$ [1], $Sr_4[MoN_4]O$ [2], $(Li_2Ca_4O)_3[WN_4]_4$ [1], $Ca_{51}[WN_4]_{12}N_8O_3$ [3], and $Sr_{51}[WN_4]_{12}N_8O_3$ [3]. Predominant structural features of the above mentioned compounds are isolated complex tetrahedral nitridometalate anions $[MN_4]^{6-}$, as well as oxide ions which are octahedrally coordinated by alkali and alkaline earth cations.

The crystal structure of $Ca_5[WN_4]O_2$ exhibits additional features: the isolated nitridotungstate anions $[WN_4]^{6-}$ (d(W—N) = 1.881 Å) are located within the holes of a matrix of two-dimensional-infinite corrugated layers of alternating OCa_5 tetragonal pyramids (d(Ca—O) = 2.450 Å) and OCa_6 octahedra (d(Ca—O): 2.399 Å) which are connected via common corners and edges. The stacking sequence of the layers (along [100]) is ...AA.... Thereby one tetrahedral plane of each $[WN_4]$-tetrahedron is nearly parallel to the basal plane of the OCa_5 tetragonal pyramid. Three independent Ca sites are irregularely coordinated (CN: 5-7) by N ($\bar{d}$(Ca—N): 2.627 Å) and O ($\bar{d}$(Ca—O): 2.422 Å). All interatomic distances are in good agreement with data from literature ($\bar{d}$(W—N): 1.884A [1], 1.884 Å [3], 1.873 Å [4]; $\bar{d}$(Ca—O): 2.327 Å [1], 2.367 Å [3], 2.406 Å [5]; $\bar{d}$(Ca—N): 2.558 Å [1], 2.546 Å [3], 2.559 Å [4]).

Table 1. Data collection and handling.

Crystal:	yellow, tetragonal prism, size 0.1 × 0.2 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	197.92 cm^{-1}
Diffractometer, scan mode:	Stoe Stadi 4, ω/θ
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2242, 1115
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1096
$N(param)_{refined}$:	68
Programs:	SHELXS-97 [6], SHELXL-97 [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	2e	0.71611(3)	1/4	0.68220(2)	0.0035(1)	0.0037(1)	0.0020(1)	0	–0.00003(7)	0
Ca(1)	4f	0.7198(1)	0.0028(1)	0.34508(9)	0.0081(3)	0.0054(4)	0.0059(3)	–0.0011(3)	0.0007(3)	0.0022(3)
Ca(2)	2e	0.1819(2)	1/4	0.3285(1)	0.0055(4)	0.0061(5)	0.0038(4)	0	–0.0004(4)	0
Ca(3)	2a	0	0	0	0.0063(4)	0.0049(5)	0.0050(4)	0.0004(4)	0.0009(3)	–0.0011(3)
Ca(4)	2e	0.5220(2)	1/4	0.0276(1)	0.0053(4)	0.0068(5)	0.0038(4)	0	–0.0001(4)	0

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Table 2. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	2*e*	0.5042(8)	1/4	0.5245(5)	0.006(2)	0.008(2)	0.003(2)	0	–0.002(2)	0
N(2)	4*f*	0.6610(6)	0.0262(5)	0.8104(4)	0.009(1)	0.004(1)	0.006(1)	–0.001(1)	–0.000(1)	0.000(1)
N(3)	2*e*	0.9774(9)	1/4	0.5747(6)	0.011(2)	0.028(3)	0.006(2)	0	0.002(2)	0
O(1)	2*e*	0.8506(7)	1/4	0.1727(5)	0.011(2)	0.015(2)	0.012(2)	0	0.003(2)	0
O(2)	2*e*	0.2056(8)	1/4	0.8795(6)	0.014(2)	0.018(2)	0.016(2)	0	–0.000(2)	0

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