Crystal structure of dibarium calcium [tetranitridotungstate(VI)], $Ba_2Ca[WN_4]$

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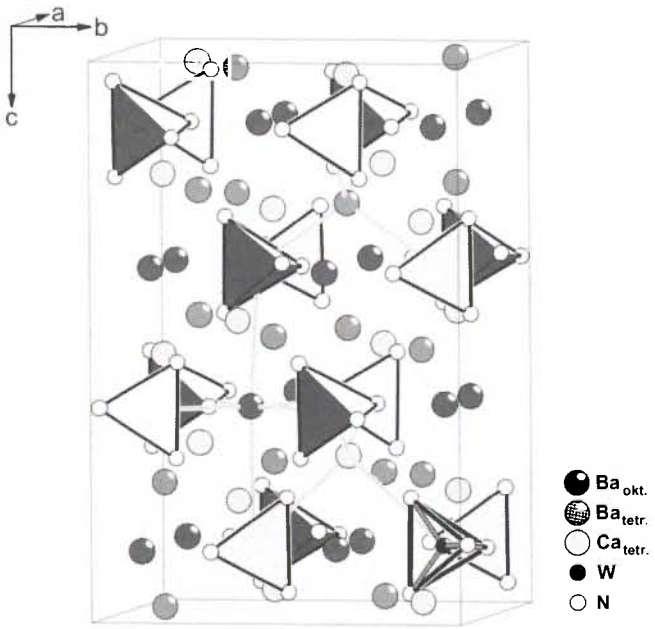
Received December 17, 1999, CSD-No. 409472



Abstract

Ba_2CaN_4W, orthorhombic, *Fddd* (No. 70), $a = 10.873(1)$ Å, $b = 11.993(1)$ Å, $c = 17.937(2)$ Å, $V = 2339.0$ Å^3, $Z = 16$, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.107$, $T = 293$ K.

Source of material

Yellow single crystals were obtained by reaction of pellets of Ca_3N_2, Ba_2N and W (molar ration 1:2:1). The reaction was carried out under N2 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

The crystal structures of several ternary alkaline earth nitridotungstates with $A_3[WN_4]$ composition have been reported in recent years: $Sr_3[WN_4]$ [1], LT-$Ba_3[WN_4]$ [2], HT-$Ba_3[WN_4]$ [1, 3], and $Ca_2Sr[WN_4]$ [4]. Predominant structural features of these compounds are isolated complex tetrahedral nitridotungstate anions $[WN_4]^{6-}$. The above mentioned crystal structures are related to the Na_3As-type structure with the complex anions in a hexagonal close packing arrangement. The tetrahedral holes are occupied by 2/3 of the alkaline earth cations, the remaining alkaline earth cations are in a trigonal planar coordination by the complex anions.

The crystal structure of $Ba_2Ca[WN_4]$ is related to the Li_3Bi-type structure with the complex anions in a cubic close packing arrangement; all octahedral holes as well as half of the tetrahedral holes are occupied by Ba, the remaining tetrahedral holes are occupied by Ca; no disorder is observed. W is tetrahedrally coordinated by N ($\bar{d}$(W—N) = 1.879 Å), Ca is octahedrally coordinated by N ($\bar{d}$(Ca—N) = 2.551 Å) and the corrdination polyhedra around Ba are irregular (CN: 8; $\bar{d}$(Ba—N) = 3.057 Å). These values are in good agreement with data from literature: $\bar{d}$(W—N) = 1.902 Å (LT-$Ba_3[WN_4]$ [2]), 1.882 Å (HT-$Ba_3[WN_4]$ [3], 1.873 Å ($Ca_2Sr[WN_4]$ [4]; $\bar{d}$(Ca—N) = 2.594 Å ($Ca_2Sr[WN_4]$ [4]; d(Ba—N) = 2.893 Å (LT-$Ba_3[WN_4]$ [2]), 2.916 Å (HT-$Ba_3[WN_4]$ [3]).

Table 1. Data collection and handling.

Crystal:	yellow, irregular, size 0.1 × 0.1 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	337.02 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω/2θ
$2\theta_{max}$:	60.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3647, 865
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 707
$N(param)_{refined}$:	40
Programs:	SHELXS-97 [5], SHELXL-97 [5], DIAMOND [6]

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)	16*f*	1/8	0.88263(3)	5/8	0.0069(3)	0.0068(3)	0.0000(3)	0	0.0001(1)	0
Ba(1)	16*g*	1/8	1/8	0.51380(4)	0.0135(4)	0.0113(3)	0.0006(3)	–0.0016(2)	0	0
Ba(2)	16*e*	0.05485(6)	7/8	7/8	0.0103(4)	0.0105(3)	0.0094(4)	0	0	0.0011(2)
Ca(1)	16*g*	1/8	1/8	0.2857(1)	0.0101(9)	0.0107(8)	0.0000(9)	–0.0019(7)	0	0
N(1)	32*h*	0.1154(7)	0.9580(7)	0.0398(5)	0.020(3)	0.020(3)	0.012(3)	0.003(3)	0.001(3)	0.012(3)
N(2)	32*h*	0.0145(6)	0.0257(6)	0.3833(4)	0.009(2)	0.012(3)	0.007(3)	0.005(3)	–0.002(2)	–0.003(2)

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Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this work.

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