Crystal structure of the high temperature phase of tribarium [tetranitridotungstate(VI)], HT-$Ba_3[WN_4]$

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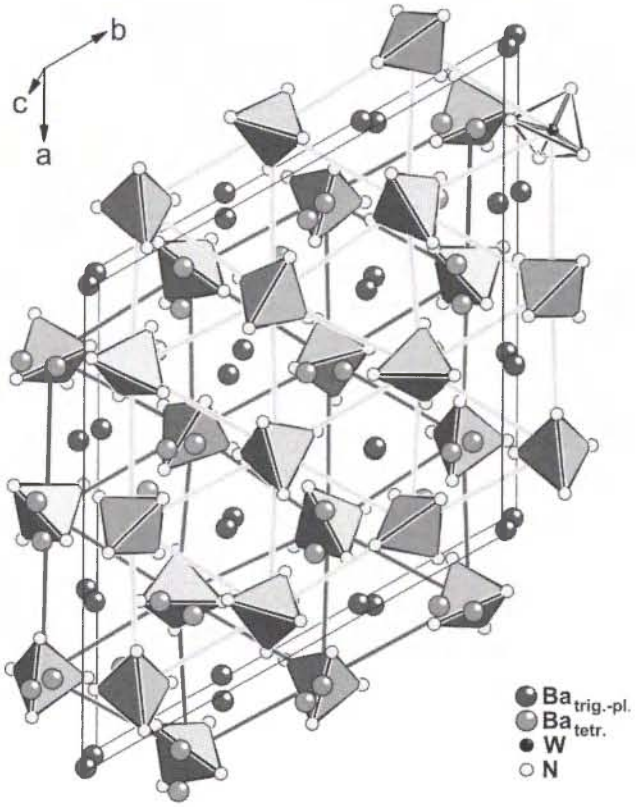

Abstract

Ba_3N_4W, trigonal, $P31c$ (No. 159), a = 18.473(2) Å, c = 10.427(1) Å, V = 3081.6 Å^3, Z = 18, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.097, T = 293 K.

Source of material

Orange-colored single crystals were obtained by reaction of pellets of Ba_2N and W (molar ratio 3:1). The reaction was carried out under N_2 of ambient pressure in W crucibles. The mixtures were heated to 1323 K (100 K/h). After a period of 36 h the products were cooled down (20 K/h) to ambient temperature. Starting materials and products are sensitive to moisture and air.

Discussion

The crystal structures of several ternary alkaline earth nitridomolybdates and -tungstates with $A_3[MN_4]$ composition are known up to now: the isotypes $Sr_3[MoN_4]$ [1, 2] and $Sr_3[WN_4]$ [1], the isotypes LT-$Ba_3[MoN_4]$ [3] and LT-$Ba_3[WN_4]$ [3], and $Ca_2Sr[WN_4]$ [4]. Predominant structural features of these compounds are isolated complex tetrahedral nitridomolybdate and nitridotungstate anions $[MN_4]^{6-}$. 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 structures of the isotypes HT-$Ba_3[WN_4]$ and HT-$Ba_3[MoN_4]$ [1, 5] are also members of this structure family; the most obvious differences refer to the orientation of the complex anions and the resulting differences in nitrogen coordination polyhedra around the alkaline earth cations. W is tetrahedrally coordinated by N ($\bar{d}$(W—N) = 1.882 Å), the coordination polyhedra of Ba are irregular (CN: 6-7; d(Ba—N)= 2.916 Å). Both values are in good agreement with data from literature: d(W—N) = 1.902 Å (LT-$Ba_3[WN_4]$ [3]), 1.873 Å ($Ca_2Sr[WN_4]$ [4]), 1.879 Å ($Ba_2Ca[WN_4]$ [5]); $\bar{d}$(Ba—N) = 2.893 Å (LT-$Ba_3[WN_4]$ [3]), 3.057 Å ($Ba_2Ca[WN_4]$ [6]).

Table 1. Data collection and handling.

Crystal:	orange-colored hexagonal prism, size 0.02 × 0.06 × 0.06 mm
Wavelength:	Mo K_α radiation (0.71070 Å)
μ:	336.62 cm^{-1}
Diffractometer, scan mode:	Siemens R3/V, Wyckoff
$2\theta_{max}$:	55.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2671, 1372
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1155
$N(param)_{refined}$:	157
Programs:	SHELXS-97 [7], SHELXL-97 [7], DIAMOND [8]

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

Atom	Site	x	y	z	U_{iso}
N(1)	6c	0.010(3)	0.153(3)	0.323(5)	0.03(1)
N(2)	6c	0.390(2)	0.271(2)	0.452(4)	0.022(9)
N(3)	6c	0.071(2)	0.270(2)	0.112(4)	0.021(9)
N(4)	6c	0.358(2)	0.529(2)	0.219(4)	0.013(7)
N(5)	6c	0.186(2)	0.528(3)	0.400(4)	0.019(8)
N(6)	6c	0.356(2)	0.163(3)	0.205(4)	0.023(9)
N(7)	6c	0.425(3)	0.484(3)	0.449(5)	0.03(1)
N(8)	6c	0.027(3)	0.455(3)	0.213(5)	0.03(1)
N(9)	6c	0.184(2)	0.308(2)	0.349(4)	0.012(7)
N(10)	6c	0.484(2)	0.173(2)	0.411(4)	0.015(8)
N(11)	6c	0.148(4)	0.165(4)	0.152(6)	0.06(2)
N(12)	6c	0.524(2)	0.326(2)	0.235(4)	0.010(7)

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Table 3. 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}
Ba(1)	2*a*	0	0	1/4[a]	0.015(1)	U_{11}	0.025(3)	$U_{11}/2$	0	0
Ba(2)	2*b*	1/3	2/3	0.3008(7)	0.015(1)	U_{11}	0.025(3)	$U_{11}/2$	0	0
Ba(3)	2*b*	2/3	1/3	0.3326(7)	0.017(1)	U_{11}	0.021(3)	$U_{11}/2$	0	0
Ba(4)	6*c*	0.3283(2)	0.0192(2)	0.3465(7)	0.014(1)	0.016(1)	0.028(2)	0.007(1)	0.002(1)	–0.000(1)
Ba(5)	6*c*	0.3329(2)	0.3509(2)	0.2179(8)	0.026(2)	0.023(2)	0.041(2)	0.015(2)	0.007(2)	0.003(2)
Ba(6)	6*c*	0.2203(2)	0.0820(2)	0.0662(7)	0.016(1)	0.013(1)	0.014(2)	0.008(1)	0.002(1)	–0.001(1)
Ba(7)	6*c*	0.2275(2)	0.1528(2)	0.4091(7)	0.015(1)	0.016(1)	0.012(2)	0.008(1)	0.001(1)	–0.000(1)
Ba(8)	6*c*	0.1874(2)	0.4375(2)	0.1483(7)	0.015(1)	0.013(1)	0.014(1)	0.006(1)	–0.002(1)	–0.001(1)
Ba(9)	6*c*	0.5189(2)	0.1249(2)	0.1422(7)	0.018(2)	0.019(1)	0.011(1)	0.009(1)	0.001(1)	–0.001(1)
Ba(10)	6*c*	0.5289(2)	0.4296(2)	0.4846(7)	0.012(1)	0.016(1)	0.014(1)	0.006(1)	0.001(1)	0.001(1)
Ba(11)	6*c*	0.2644(2)	0.4483(2)	0.4887(8)	0.015(1)	0.015(1)	0.016(2)	0.007(1)	–0.002(1)	–0.001(1)
W(1)	6*c*	0.1049(1)	0.2256(1)	0.2311(7)	0.0114(9)	0.0128(9)	0.011(1)	0.0070(8)	0.0010(8)	0.0003(8)
W(2)	6*c*	0.1098(1)	0.5493(1)	0.3206(7)	0.0099(8)	0.0106(8)	0.017(1)	0.0045(7)	–0.0016(8)	0.0014(8)
W(3)	6*c*	0.4400(1)	0.2364(1)	0.3254(7)	0.0116(9)	0.0129(9)	0.012(1)	0.0065(8)	–0.0023(8)	–0.0004(8)

a: fixed for definition of the origin

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References

1. Höhn, P.; Gudat, A.; Kniep, R.; Maier, J.: Preparation and crystal chemistry of nitridomolybdates (VI) and nitridotungstates (VI); ECSSC IV, A 56, Dresden, Germany 1992.
2. Höhn, P.; Kniep, R.: Crystal structure of tristrontium [tetranitridomolybdate(VI)], $Sr_3[MoN_4]$. Z. Kristallogr. NCS **215** (2000) 325-326.
3. Gudat, A.; Höhn, P.; Kniep, R.; Rabenau, A.: The crystal structures of the isotypic compounds $Ba_3[MoN_4]$ and $Ba_3[WN_4]$. Z. Naturforsch. **46b** (1991) 566-572.
4. Berger, U.; Schultz-Coulon, V.; Schnick, W.: $Ca_2Sr[WN_4]$, the first mixed alkaline earth nitridotungstate. Z. Naturforsch. **50b** (1995) 213-216.
5. Höhn, P.; Kniep, R.: Crystal structure of the high temperature phase of tribarium [tetranitridomolybdate(VI)], HT-$Ba_3[MoN_4]$. Z. Kristallogr. NCS **215** (2000) 327-328.
6. Höhn, P.; Kniep, R.: Crystal structure of dibarium calcium [tetranitridotungstate(VI)], $Ba_2Ca[WN_4]$. Z. Kristallogr. NCS **215** (2000) 331-332.
7. Sheldrick, G. M.: SHELXL-97, a program for refining crystal structures. University of Göttingen, Germany 1997.
8. Brandenburg, K.: Diamond (Version 2.1a). Crystal Impact GbR, Germany 1996-1999.