Crystal structure of the high temperature phase of tribarium [tetranitridomolybdate(VI)], HT-$Ba_3[MoN_4]$

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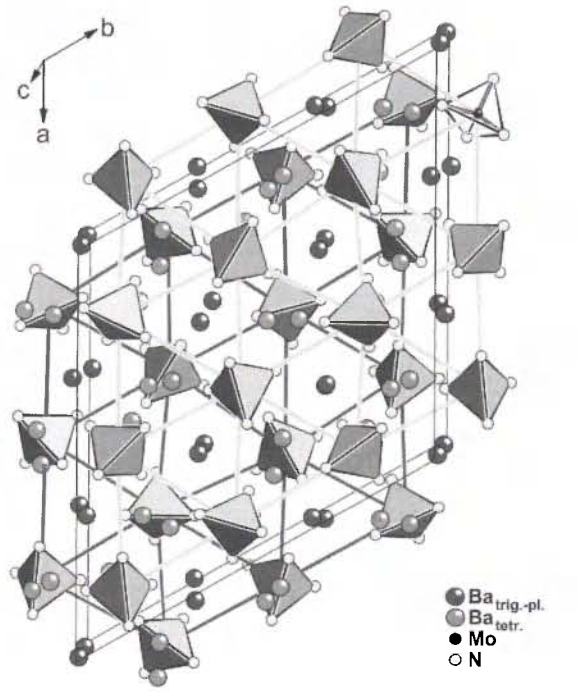

Abstract

Ba_3MoN_4, trigonal, $P31c$ (No. 159), a = 18.441(5) Å, c = 10.401(3) Å, V = 3063.3 Å^3, Z = 18, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.078, T = 293 K.

Source of material

Yellow single crystals were obtained by reaction of pellets of Ba_2N and Mo (molar ratio 3:1). The reaction was carried out under N_2 at ambient pressure in Mo 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 forming 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-$Ba_3[MoN_4]$ and HT-$Ba_3[WN_4]$ [1, 5] are also members of this structure family; the most obvious differences between the different crystal structures refer to the orientation of the complex anions and the resulting differences in nitrogen coordination polyhedra of the alkaline earth cations. Mo is tetrahedrally coordinated by N ($\bar{d}$(Mo—N) = 1.864 Å), the coordination polyhedra of Ba are irregular (CN: 5-7; $\bar{d}$(Ba—N) = 2.919 Å). Both values are in good agreement with data from literature: $\bar{d}$(Mo—N) = 1.867 Å (LT-$Ba_3[MoN_4]$ [3]), 1.867 Å ($Sr_3[MoN_4]$ [2]); $\bar{d}$(Ba—N) = 2.893 Å (LT-$Ba_3[MoN_4]$ [3]), 2.916 Å (HT-$Ba_3[WN_4]$ [5]), 3.057 Å ($Ba_2Ca[WN_4]$ [6]).

Table 1. Data collection and handling.

Crystal:	yellow, hexagonal prism, size 0.04 × 0.2 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71070 Å)
μ:	188.21 cm^{-1}
Diffractometer, scan mode:	Siemens R3/V, Wyckoff
$2\theta_{max}$:	55.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5038, 2585
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2289
$N(param)_{refined}$:	218
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_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	2*a*	0	0	1/4[a]	0.0178(6)	U_{11}	0.030(1)	$U_{11}/2$	0	0
Ba(2)	2*b*	1/3	2/3	0.2992(3)	0.0185(6)	U_{11}	0.027(1)	$U_{11}/2$	0	0
Ba(3)	2*b*	2/3	1/3	0.3321(3)	0.0217(6)	U_{11}	0.027(1)	$U_{11}/2$	0	0
Ba(4)	6*c*	0.32772(8)	0.01895(8)	0.3444(2)	0.0179(6)	0.0202(5)	0.0266(6)	0.0078(5)	0.0019(4)	0.0017(4)
Ba(5)	6*c*	0.33170(9)	0.34941(9)	0.2182(3)	0.0284(7)	0.0253(7)	0.0513(9)	0.0149(6)	0.0072(6)	0.0034(6)

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Table 2. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(6)	6c	0.21973(7)	0.08192(7)	0.0646(2)	0.0193(6)	0.0160(5)	0.0162(6)	0.0091(5)	–0.0001(4)	–0.0007(4)
Ba(7)	6c	0.22744(7)	0.15245(8)	0.4086(3)	0.0189(6)	0.0200(6)	0.0162(6)	0.0100(5)	–0.0003(4)	0.0002(4)
Ba(8)	6c	0.18671(7)	0.43756(7)	0.1471(3)	0.0182(6)	0.0157(5)	0.0164(5)	0.0079(4)	–0.0010(4)	–0.0006(4)
Ba(9)	6c	0.51879(7)	0.12439(7)	0.1409(2)	0.0200(6)	0.0214(6)	0.0160(5)	0.0109(5)	0.0008(4)	0.0002(4)
Ba(10)	6c	0.52855(7)	0.42897(7)	0.4830(2)	0.0170(5)	0.0177(5)	0.0189(5)	0.0079(5)	0.0001(4)	–0.0003(4)
Ba(11)	6c	0.26440(7)	0.44939(7)	0.4887(3)	0.0195(6)	0.0206(6)	0.0178(5)	0.0100(5)	–0.0023(4)	–0.0006(4)
Mo(1)	6c	0.1054(1)	0.2266(1)	0.2299(3)	0.0151(8)	0.0151(8)	0.0136(8)	0.0076(6)	0.0002(6)	–0.0003(6)
Mo(2)	6c	0.1096(1)	0.5497(1)	0.3184(3)	0.0152(8)	0.0161(8)	0.0179(8)	0.0081(6)	0.0001(6)	0.0024(6)
Mo(3)	6c	0.4402(1)	0.2360(1)	0.3238(3)	0.0153(7)	0.0138(7)	0.0163(8)	0.0063(6)	–0.0005(6)	0.0007(6)
N(1)	6c	0.012(1)	0.153(1)	0.325(1)	0.03(1)	0.029(9)	0.001(7)	0.011(8)	0.001(6)	0.005(6)
N(2)	6c	0.392(1)	0.272(1)	0.445(2)	0.023(9)	0.030(9)	0.015(8)	0.018(8)	0.004(6)	0.003(6)
N(3)	6c	0.0707(9)	0.274(1)	0.103(2)	0.008(7)	0.021(9)	0.019(9)	–0.005(7)	0.005(6)	–0.005(7)
N(4)	6c	0.356(1)	0.524(1)	0.219(2)	0.024(9)	0.022(9)	0.04(1)	0.009(8)	0.000(7)	–0.006(7)
N(5)	6c	0.188(1)	0.527(1)	0.397(2)	0.016(8)	0.031(9)	0.019(8)	0.009(7)	0.006(6)	–0.002(7)
N(6)	6c	0.361(1)	0.163(1)	0.204(2)	0.014(8)	0.023(9)	0.04(1)	0.003(7)	–0.006(7)	–0.006(8)
N(7)	6c	0.422(1)	0.481(1)	0.448(1)	0.03(1)	0.026(9)	0.021(8)	0.026(8)	0.007(7)	0.016(7)
N(8)	6c	0.036(1)	0.459(1)	0.212(2)	0.022(9)	0.021(9)	0.06(1)	0.012(8)	–0.013(8)	0.001(8)
N(9)	6c	0.1842(9)	0.313(1)	0.339(2)	0.007(7)	0.024(9)	0.020(8)	–0.001(6)	0.005(6)	–0.006(7)
N(10)	6c	0.484(1)	0.176(1)	0.400(2)	0.04(1)	0.04(1)	0.026(9)	0.03(1)	–0.003(8)	–0.002(8)
N(11)	6c	0.154(1)	0.172(2)	0.152(2)	0.06(1)	0.07(2)	0.013(9)	0.06(1)	0.008(9)	0.004(9)
N(12)	6c	0.525(1)	0.326(1)	0.236(2)	0.03(1)	0.03(1)	0.011(8)	0.011(8)	–0.002(7)	–0.005(7)

a: fixed for definition of the origin

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