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Preparation and structural characterisation of the trigonal nitridometalate Ba_3MoN_4

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The preparation and structural characterisation of a high temperature trigonal modification of Ba_3MoN_4 is described and compared to the previously reported orthorhombic form. The trigonal form was prepared by the reaction of barium nitride and molybdenum metal foil at 1393 K for 5 days in sealed stainless steel crucibles under argon. The structure is characterised by the presence of isolated $[MoN_4]^{6-}$ tetrahedra which are stacked along the *c* axis. The structural analogies and differences between the two forms of Ba_3MoN_4 are discussed and their relationship to the $AMoO_4$ (A = Ca, Sr, Ba) compounds with the scheelite structure, which represents the family of oxides most structurally related to the Ba–Mo–N nitrides.

Introduction

In recent years ternary nitrides have gained increasing importance in the search for materials as alternatives to oxides for technological applications owing to the fact that N^{3-} is similar to O^{2-} with respect to size, polarisability and electronegativity. Our knowledge base of oxide materials is clearly extensive and has led to their classification, based on structural types, to be well established and we now have a good degree of insight into the structure–properties relationships of many multinary oxides. The discovery of new nitrides, which is now happening at an appreciable speed, has already allowed researchers to delineate broad structural classes of ternary nitrides[1] and in the not-too-distant future should lead to a deeper understanding of the structural relationships between ternary nitrides and ternary oxides, and therefore to better awareness of the technological potential of ternary nitrides.

In transition metal ternary nitrides, transition metals display a wealth of coordination numbers and oxidation states, sometimes similar to but frequently different from those that they assume in ternary oxide compounds. First row transition metals on the right hand side of the periodic table such as Cu, Zn, Fe, Co, Ni tend to form ternary nitrides in which they adopt low oxidation states and to show multiple bonds and low coordination numbers with nitrogen.[2] On the other hand, transition metals such as Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W, prefer higher oxidation states and higher coordination numbers.[2] Most of the ternary nitrides with transition metals in high oxidation states can be described as nitridometalates as they share many similarities with the corresponding oxo-compounds and can therefore be considered the most promising alternative to oxides. Nitridometalates usually contain isolated monomeric or oligomeric $M_xN_y{}^{n-}$ units and electropositive counter ions, such as alkali or alkaline-earth cations.

Alkali and alkaline-earth molybdenum nitrides, A–Mo–N [A = Li, (Li, Ba), Ba, (Ca, Sr)], have been known for a long time. In these compounds Mo is usually in its maximum oxidation state (6+), tetrahedrally coordinated by nitrogen and can be present in the form of isolated $[MoN_4]^{6-}$ tetrahedra, dimeric $[Mo_2N_7]^{9-}$ or polymeric $[Mo_2N_2N_{2/2}]^{3-}$ units.[3] In 1991 Gudat *et al.*[4] reported the preparation and structural characterisation of single crystals of the orthorhombic Ba_3MoN_4 with lattice constants $a = 10.839(3)$, $b = 10.303(3)$ and $c = 12.029(3)$ Å. Here, we report the preparation and structural characterisation of a trigonal modification of Ba_3MoN_4 with lattice constants $a = 18.422(3)$ and $c = 10.405(3)$ Å. Both structural modifications show interesting frameworks resulting from the arrangement of isolated $[MoN_4]^{6-}$ tetrahedra. We discuss some structural analogies and differences between the two Ba_3MoN_4 phases and then we extend the comparison to the $AMoO_4$ oxides with the scheelite structure, which contain Mo–O isolated tetrahedra and can therefore be considered structurally similar to alkali and alkaline-earth Mo ternary nitrides. We also describe in detail our synthetic route which allowed us to obtain single crystals sufficiently large for X-ray diffraction studies.

After the completion of this work it came to our attention that the structural characterisation of the trigonal modification of Ba_3MoN_4, although not reported in the open literature, was previously presented in a PhD thesis.[5]

Experimental

Ba_3MoN_4 single crystals were prepared by reacting Ba_2N with Mo metal. Ba_2N was prepared by dissolving Ba in an excess of molten Na and reacting it with nitrogen gas.[6] Ba_3MoN_4 crystals were grown on Mo foils. Finely ground powder of Ba_2N was put in a liner made from Mo foil. The Mo liner was then put into a stainless steel crucible which was subsequently welded closed. Ba_2N is extremely air and moisture-sensitive, thus all operations were carried out in an argon-filled glove box to avoid any contact of Ba_2N with air. The sample was heated at 1120 °C for 5 days in a tube furnace under flowing argon to minimise external aerial oxidation of the crucible. It was then cooled to room temperature at 0.3 °C min^{-1}. The crucible was cut open in an argon-filled glove box. Single crystals of Ba_3MoN_4 were found to have grown on the Mo liner walls. The best crystals were separated from the batch and put into glass capillaries. The open end of the capillary was sealed with a plug of grease to prevent any contact with air/moisture when the capillary was taken out of the Ar-filled glove box to be flame sealed. The capillary was then broken under RS3000 (Riedel de Haen) oil, a highly viscous perfluoropolyether that is moisture free. This protected the crystals suffiicently long for optical examination in the open air and subsequent loading onto the diffractometer. When cooled to 150 K for data collection the oil freezes around the crystal and locks it into position. Single-crystal X-ray

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data were collected using a Stöe STADI4 four-circle diffractometer equipped with an Oxford Cryo Systems open-flow cryostat operating at 150 K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The shape of the crystals and their chemical composition were analysed with a JEOL 6400 WINSEM scanning electron microscope (SEM) coupled with a Noram/Tracor series II EDX analyser.

Structure determination

A red/black crystal of dimensions 0.23 × 0.15 × 0.116 mm was used for structure determination. Data were collected at 150 K.

The structure was solved by direct methods in the non-centrosymmetric space group *P*31*c* (no. 159). The unit cell dimensions were refined using 57 independent reflections in the range $21 \leq 2\theta \leq 35°$. The structure determination and full-matrix least-square refinement were carried out using the WINGX package[7] and a numerical absorption correction was made using DIFABS.[8] The structure was solved using 1716 reflections with $I > 2\sigma(I)$. The function minimised in the least-square refinement was $\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2$.

The refinement on F^2 was performed against all reflections. Anisotropic refinement of all Ba and Mo cations and of the N1, N2, N5, N7, N10 anions converged to $R = 0.0488$ and $R' = 0.0444$. The weighted *R*-factor, *wR*, and goodness of fit *S*, ($wR = 0.1107$; $S = 1.079$) are based on F^2, conventional *R*-factors, *R*, are based on *F* with *F* set to zero for negative F^2.

Crystal data and details are given in Table 1 selected bond distances in Table 2 and selected bond angles in Table 3.

CCDC reference number 186/1937.

See http://www.rsc.org/suppdata/dt/a9/a908546g/ for crystallographic files in .cif format.

Results and discussion

The reaction of the Group 2 binary nitrides with transition metals always requires high temperature in order to achieve the formation of single phase products. Previous work at Nottingham has indicated that the growth of single crystals is favored when the Group 2 nitride is in contact with a transition metal in the form of a thin foil. The melting point of barium nitride is not known but complete melting of the binary nitride would promote its reactivity towards Mo metal and increase the chance of single crystal formation. Similarly the rolling process used to produce a thin foil leads to deformation of the crystallites on the metal surface and the enhanced reactivity of the grain boundaries which could also act as sites for crystal growth of the ternary nitride. Thus in our experimental system when the temperature reaches 1120 °C, Ba_2N may melt and react with the surrounding Mo metal foil leading to the formation of nuclei of Ba_3MoN_4 crystals which subsequently grow on the wall of the Mo liner. The cooling of the molten phase to room temperature appears to be an important step for the growth of nuclei into single crystals since a very slow cooling step favours the formation of large and regularly shaped crystals. In our synthetic strategy the cooling rate was 0.3 °C min^{-1} and this led to the formation of good size single crystals.

Table 1 Crystal data and structure refinement for the trigonal Ba_3MoN_4

Chemical formula	Ba_3MoN_4
Formula weight	10152.00
Crystal system	Trigonal
Space group	*P*31*c*
μ/mm^{-1}	18.852
R Values	$R1 = 0.0488$; $wR2 = 0.1124$
Unit cell dimensions	$a,b = 18.422(3)$ Å; $c = 10.405(2)$ Å $\alpha, \beta = 90°$; $\gamma = 120°$
Unit cell volume/Å^3	3058.1(9)
Temperature of data collection/K	150
Z	18
Measured/independent reflections and *R*(int)	$R1 = 0.0444$ for 1716 $F_o > 4\sigma(F_o)$ and 0.0488 for all 1798 data

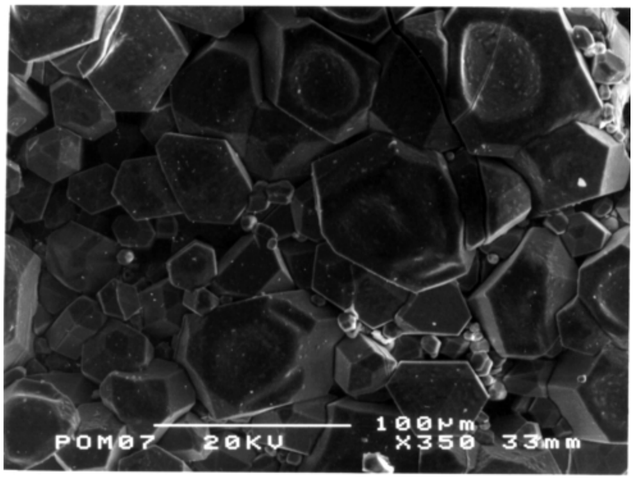

Fig. 1 SEM image of crystals of the trigonal Ba_3MoN_4.

The SEM image in Fig. 1 shows a large number of crystals of the trigonal Ba_3MoN_4 on a piece of Mo foil: their hexagonal habit is clearly visible. Care was taken in trying to minimise the exposure to air when the crystals were transferred into the vacuum chamber of the SEM/EDX apparatus. Nevertheless, signs of initial decomposition are clearly visible (Fig. 1), given that Ba_3MoN_4, like the majority of ternary nitrides, is extremely air- and moisture-sensitive.

EDX analyses proved fundamental in determining the composition of the crystals. From the analysis of a large number of individual crystals we found an average Ba : Mo atomic ratio of 75 : 25, and this result, together with the structural data, indicated that the chemical formula of our compound is Ba_3MoN_4.

Table 2 Selected bond lengths (Å) for the trigonal Ba_3MoN_4

Mo(1)–N(1)	1.83(3)	Ba(1)–N(6)	3.08(2)	Ba(5)–N(12)	2.64(3)	Ba(9)–N(10)	2.85(3)
Mo(1)–N(7)	1.87(2)	Ba(2)–N(11)	2.79(2)	Ba(5)–N(8)	2.66(3)	Ba(9)–N(3)	2.87(2)
Mo(1)–N(3)	1.88(2)	Ba(2)–N(5)	3.06(3)	Ba(5)–N(11)	2.70(2)	Ba(9)–N(9)	2.88(2)
Mo(1)–N(9)	1.88(2)	Ba(3)–N(1)	2.72(3)	Ba(5)–N(9)	2.85(2)	Ba(9)–N(4)	3.11(2)
Mo(2)–N(12)	1.84(2)	Ba(3)–N(2)	2.77(2)	Ba(5)–N(7)	2.87(2)	Ba(9)–N(6)	3.23(2)
Mo(2)–N(2)	1.87(3)	Ba(3)–N(6)	2.78(2)	Ba(5)–N(5)	3.06(3)	Ba(9)–N(4)	3.29(2)
Mo(2)–N(4)	1.88(2)	Ba(3)–N(4)	2.85(2)	Ba(6)–N(6)	2.75(2)	Ba(10)–N(7)	2.62(2)
Mo(2)–N(8)	1.92(3)	Ba(3)–N(2)	3.00(2)	Ba(6)–N(2)	3.32(3)	Ba(10)–N(10)	2.65(3)
Mo(3)–N(11)	1.83(2)	Ba(3)–N(9)	3.14(2)	Ba(7)–N(12)	2.65(3)	Ba(10)–N(11)	2.75(3)
Mo(3)–N(5)	1.85(3)	Ba(4)–N(4)	2.70(2)	Ba(7)–N(3)	2.74(2)	Ba(10)–N(12)	2.93(3)
Mo(3)–N(10)	1.88(3)	Ba(4)–N(3)	2.74(3)	Ba(7)–N(1)	2.78(3)	Ba(10)–N(3)	2.98(3)
Mo(3)–N(12)	1.90(3)	Ba(4)–N(5)	2.78(3)	Ba(7)–N(5)	2.86(3)	B(11)–N(8)	2.80(3)
Ba(1)–N(2)	2.64(3)	Ba(4)–N(1)	2.98(3)	Ba(7)–N(10)	2.93(3)	B(11)–N(5)	2.95(4)
Ba(1)–N(9)	2.67(2)	Ba(4)–N(8)	3.06(3)	Ba(7)–N(7)	3.12(2)	B(11)–N(2)	3.08(3)
Ba(1)–N(4)	2.74(2)	Ba(4)–N(10)	3.07(3)	Ba(8)–N(7)	2.77(2)	B(11)–N(12)	3.22(3)
Ba(1)–N(6)	2.87(2)	Ba(4)–N(11)	3.17(2)	Ba(8)–N(3)	3.31(2)	B(11)–N(1)	3.25(3)
Ba(1)–N(8)	2.89(3)						

Table 3 Selected angles (°) for the trigonal Ba_3MoN_4

N(1)–Mo(1)–N(7)	110.0(10)	N(5)–Ba(2)–N(5)	114.6(4)	N(11)–Ba(5)–N(7)	105.1(7)	N(3)–Ba(8)–N(3)	115.3(3)
N(1)–Mo(1)–N(3)	110.5(13)	N(5)–Ba(2)–N(5)	114.6(4)	N(9)–Ba(5)–N(7)	64.4(6)	N(7)–Ba(8)–N(3)	168.9(6)
N(7)–Mo(1)–N(3)	111.4(10)	N(1)–Ba(3)–N(2)	94.4(8)	N(12)–Ba(5)–N(5)	58.8(9)	N(7)–Ba(8)–N(3)	60.5(6)
N(1)–Mo(1)–N(9)	109.6(12)	N(1)–Ba(3)–N(12)	136.3(7)	N(8)–Ba(5)–N(5)	79.5(8)	N(7)–Ba(8)–N(3)	74.9(6)
N(7)–Mo(1)–N(9)	108.7(10)	N(2)–Ba(3)–N(12)	111.9(7)	N(11)–Ba(5)–N(5)	78.9(8)	N(3)–Ba(8)–N(3)	115.3(3)
N(3)–Mo(1)–N(9)	106.6(10)	N(1)–Ba(3)–N(4)	78.7(8)	N(9)–Ba(5)–N(5)	167.5(7)	N(3)–Ba(8)–N(3)	115.3(3)
N(12)–Mo(2)–N(2)	110.8(11)	N(2)–Ba(3)–N(4)	65.8(7)	N(7)–Ba(5)–N(5)	126.9(7)	N(23)–Ba(9)–N(3)	87.4(7)
N(12)–Mo(2)–N(4)	108.8(10)	N(12)–Ba(3)–N(4)	81.2(7)	N(12)–Ba(6)–N(12)	114.8(4)	N(23)–Ba(9)–N(9)	102.4(7)
N(2)–Mo(2)–N(4)	109.1(11)	N(1)–Ba(3)–N(2)	110.7(8)	N(12)–Ba(6)–N(12)	114.8(4)	N(3)–Ba(9)–N(9)	63.1(7)
N(12)–Mo(2)–N(8)	109.9(11)	N(2)–Ba(3)–N(2)	129.4(3)	N(12)–Ba(6)–N(12)	114.8(4)	N(23)–Ba(9)–N(4)	151.6(7)
N(2)–Mo(2)–N(8)	107.3(11)	N(12)–Ba(3)–N(2)	79.4(7)	N(12)–Ba(6)–N(2)	170.7(6)	N(3)–Ba(9)–N(4)	80.2(7)
N(4)–Mo(2)–N(8)	110.8(11)	N(4)–Ba(3)–N(2)	159.1(7)	N(12)–Ba(6)–N(2)	59.5(6)	N(9)–Ba(9)–N(4)	94.7(7)
N(11)–Mo(3)–N(5)	106.8(13)	N(1)–Ba(3)–N(9)	61.8(7)	N(12)–Ba(6)–N(2)	74.4(6)	N(23)–Ba(9)–N(12)	134.6(7)
N(11)–Mo(3)–N(10)	114.9(11)	N(2)–Ba(3)–N(9)	152.8(7)	N(12)–Ba(6)–N(2)	59.5(6)	N(3)–Ba(9)–N(12)	129.5(6)
N(5)–Mo(3)–N(10)	110.4(12)	N(12)–Ba(3)–N(9)	81.9(6)	N(12)–Ba(6)–N(2)	74.4(6)	N(9)–Ba(9)–N(12)	78.9(6)
N(11)–Mo(3)–N(12)	106.5(12)	N(4)–Ba(3)–N(9)	94.9(7)	N(12)–Ba(6)–N(2)	170.7(6)	N(4)–Ba(9)–N(12)	70.6(6)
N(5)–Mo(3)–N(12)	97.7(15)	N(2)–Ba(3)–N(9)	74.8(7)	N(2)–Ba(6)–N(2)	111.2(4)	N(23)–Ba(9)–N(4)	79.9(7)
N(10)–Mo(3)–N(12)	118.6(13)	N(4)–Ba(4)–N(3)	90.4(7)	N(12)–Ba(6)–N(2)	74.4(6)	N(3)–Ba(9)–N(4)	138.2(7)
N(2)–Ba(1)–N(9)	89.3(7)	N(4)–Ba(4)–N(5)	131.9(9)	N(12)–Ba(6)–N(2)	170.7(6)	N(9)–Ba(9)–N(4)	81.0(6)
N(2)–Ba(1)–N(4)	141.2(8)	N(3)–Ba(4)–N(5)	112.9(8)	N(12)–Ba(6)–N(2)	59.5(6)	N(4)–Ba(9)–N(4)	125.6(7)
N(9)–Ba(1)–N(4)	96.0(7)	N(4)–Ba(4)–N(1)	76.7(7)	N(2)–Ba(6)–N(2)	111.2(4)	N(12)–Ba(9)–N(4)	55.3(6)
N(2)–Ba(1)–N(12)	114.2(7)	N(3)–Ba(4)–N(1)	64.2(7)	N(2)–Ba(6)–N(2)	111.2(4)	N(7)–Ba(10)–N(23)	113.6(8)
N(9)–Ba(1)–N(12)	145.5(7)	N(5)–Ba(4)–N(1)	77.0(8)	N(12)–Ba(7)–N(3)	122.7(9)	N(7)–Ba(10)–N(11)	106.0(7)
N(4)–Ba(1)–N(12)	81.5(7)	N(4)–Ba(4)–N(8)	65.4(7)	N(12)–Ba(7)–N(1)	81.8(9)	N(23)–Ba(10)–N(11)	125.0(8)
N(2)–Ba(1)–N(8)	100.3(7)	N(3)–Ba(4)–N(8)	151.9(7)	N(3)–Ba(7)–N(1)	138.2(8)	N(7)–Ba(10)–N(12)	84.4(8)
N(9)–Ba(1)–N(8)	87.2(7)	N(5)–Ba(4)–N(8)	77.6(9)	N(12)–Ba(7)–N(5)	113.5(10)	N(23)–Ba(10)–N(12)	83.7(8)
N(4)–Ba(1)–N(8)	118.3(7)	N(1)–Ba(4)–N(8)	94.9(7)	N(3)–Ba(7)–N(5)	113.3(9)	N(11)–Ba(10)–N(12)	63.4(8)
N(12)–Ba(1)–N(8)	64.8(7)	N(4)–Ba(4)–N(23)	86.4(7)	N(1)–Ba(7)–N(5)	79.1(9)	N(7)–Ba(10)–N(3)	83.0(7)
N(2)–Ba(1)–N(12)	80.1(7)	N(3)–Ba(4)–N(23)	86.0(7)	N(12)–Ba(7)–N(23)	83.7(8)	N(23)–Ba(10)–N(3)	89.1(7)
N(9)–Ba(1)–N(12)	84.9(7)	N(5)–Ba(4)–N(23)	134.3(8)	N(3)–Ba(7)–N(23)	88.8(7)	N(11)–Ba(10)–N(3)	133.4(7)
N(4)–Ba(1)–N(12)	62.3(7)	N(1)–Ba(4)–N(23)	145.2(7)	N(1)–Ba(7)–N(23)	130.1(8)	N(12)–Ba(10)–N(3)	161.6(8)
N(12)–Ba(1)–N(12)	122.4(3)	N(8)–Ba(4)–N(23)	105.5(7)	N(5)–Ba(7)–N(23)	63.9(8)	N(8)–Ba(11)–N(5)	79.2(7)
N(8)–Ba(1)–N(12)	172.1(7)	N(4)–Ba(4)–N(11)	123.7(7)	N(12)–Ba(7)–N(7)	105.3(8)	N(8)–Ba(11)–N(2)	62.4(7)
N(11)–Ba(2)–N(11)	106.7(6)	N(3)–Ba(4)–N(11)	126.6(7)	N(3)–Ba(7)–N(7)	78.5(7)	N(5)–Ba(11)–N(2)	128.3(7)
N(11)–Ba(2)–N(11)	106.7(6)	N(5)–Ba(4)–N(11)	75.9(7)	N(1)–Ba(7)–N(7)	61.5(7)	N(8)–Ba(11)–N(12)	82.2(8)
N(11)–Ba(2)–N(11)	106.7(6)	N(1)–Ba(4)–N(11)	152.9(7)	N(5)–Ba(7)–N(7)	118.8(7)	N(5)–Ba(11)–N(12)	54.2(8)
N(11)–Ba(2)–N(5)	77.6(7)	N(8)–Ba(4)–N(11)	80.6(7)	N(23)–Ba(7)–N(7)	167.0(7)	N(2)–Ba(11)–N(12)	140.0(8)
N(11)–Ba(2)–N(5)	60.5(7)	N(23)–Ba(4)–N(11)	60.3(7)	N(7)–Ba(8)–N(7)	108.7(5)	N(8)–Ba(11)–N(1)	93.8(7)
N(11)–Ba(2)–N(5)	167.1(7)	N(12)–Ba(5)–N(8)	96.8(9)	N(7)–Ba(8)–N(7)	108.7(5)	N(5)–Ba(11)–N(1)	120.8(7)
N(11)–Ba(2)–N(5)	60.5(7)	N(12)–Ba(5)–N(11)	131.6(9)	N(7)–Ba(8)–N(7)	108.7(5)	N(2)–Ba(11)–N(1)	96.1(6)
N(11)–Ba(2)–N(5)	167.1(7)	N(8)–Ba(5)–N(11)	97.4(8)	N(7)–Ba(8)–N(3)	60.5(6)	N(12)–Ba(11)–N(1)	66.7(7)
N(11)–Ba(2)–N(5)	77.6(7)	N(12)–Ba(5)–N(9)	121.8(8)	N(7)–Ba(8)–N(3)	74.9(6)	N(8)–Ba(11)–N(1)	94.4(7)
N(5)–Ba(2)–N(5)	114.6(4)	N(8)–Ba(5)–N(9)	88.1(7)	N(7)–Ba(8)–N(3)	168.9(6)	N(5)–Ba(11)–N(1)	70.5(8)
N(11)–Ba(2)–N(5)	167.1(7)	N(11)–Ba(5)–N(9)	104.6(7)	N(7)–Ba(8)–N(3)	74.9(6)	N(2)–Ba(11)–N(1)	79.0(6)
N(11)–Ba(2)–N(5)	77.6(7)	N(12)–Ba(5)–N(7)	85.2(8)	N(7)–Ba(8)–N(3)	168.9(6)	N(12)–Ba(11)–N(1)	124.3(8)
N(11)–Ba(2)–N(5)	60.5(7)	N(8)–Ba(5)–N(7)	147.9(7)	N(7)–Ba(8)–N(3)	60.5(6)	N(1)–Ba(11)–N(1)	167.2(7)

The same chemical formula was found for an orthorhombic ternary nitride, the structure of which had been previously characterised by Gudat *et al.*[4] However, the unit cell parameters and the space group of the two compounds are completely different: $a = 10.839(3)$, $b = 10.303(3)$, $c = 12.029(3)$ Å and space group *Pbca* (no. 88) for the orthorhombic phase, $a = b = 18.422(3)$, $c = 10.405(3)$ Å, and space group *P*31*c* (no. 159) for the trigonal phase. This indicates that the trigonal phase is a structural modification of the orthorhombic Ba_3MoN_4 ternary nitride.

There are analogies and differences between the two structural modifications. We will first concentrate on the differences between the synthetic route followed by Gudat *et al.*[4] to prepare the orthorhombic Ba_3MoN_4 and that followed by us to prepare the trigonal Ba_3MoN_4. The major differences lie in the temperature regimes and reaction times used in the two routes: the orthorhombic Ba_3MoN_4 was prepared at 900 °C for 20 h while our trigonal phase was prepared at 1120 °C for five days. The different conditions used in our synthetic route favoured the formation of the trigonal Ba_3MoN_4 modification instead of the orthorhombic one. Trigonal Ba_3MoN_4 is characterised by a much larger cell and contains more than three times the number of cations and anions than that of its orthorhombic counterpart. In fact, the unit cell of trigonal Ba_3MoN_4 represents one of the largest unit cells so far found in ternary nitrides. The higher reaction temperature and the longer reaction time adopted in our synthesis suggest that the trigonal structure represents a high temperature modification of the orthorhombic form which is stable up to at least 950 °C. In an attempt to find a possible third phase in the Ba–Mo–N system, in a lower temperature range, we prepared a powder sample by heating Ba_2N and Mo metal powder at 750 °C in a N_2 atmosphere for 50 h. The resulting product of this reaction was analysed by X-ray powder diffraction. The X-ray powder pattern showed a poorly crystallised product which consisted of a mixture of unreacted Mo metal and the orthorhombic modification of Ba_3MoN_4. This suggests that only two phases exist in the Ba–Mo–N system, orthorhombic and trigonal Ba_3MoN_4.

A [001] projection of the structure of the trigonal form of Ba_3MoN_4 is shown in Fig. 2(a) and a [010] projection of the structure of the orthorhombic form of Ba_3MoN_4[4] is shown in Fig. 2(b). In both structures Mo–N isolated tetrahedra form frameworks which constitute the backbone of the structure and Ba–N polyhedra fit within the framework itself. As shown in Fig. 2(a) and 2(b), both phases contain hexagonal patterns formed by the Mo–N isolated tetrahedra, which are stacked along the shortest axis of the unit cell: along the *b* axis in the orthorhombic phase and along the *c* axis in the trigonal phase. The hexagons are planar in orthorhombic Ba_3MoN_4 and non-planar in trigonal Ba_3MoN_4. Unlike its orthorhombic counterpart, in trigonal Ba_3MoN_4 more than one crystallographically independent Mo site is present, rendering the structure far more complex. All the hexagons formed by Mo1–N and Mo3–N

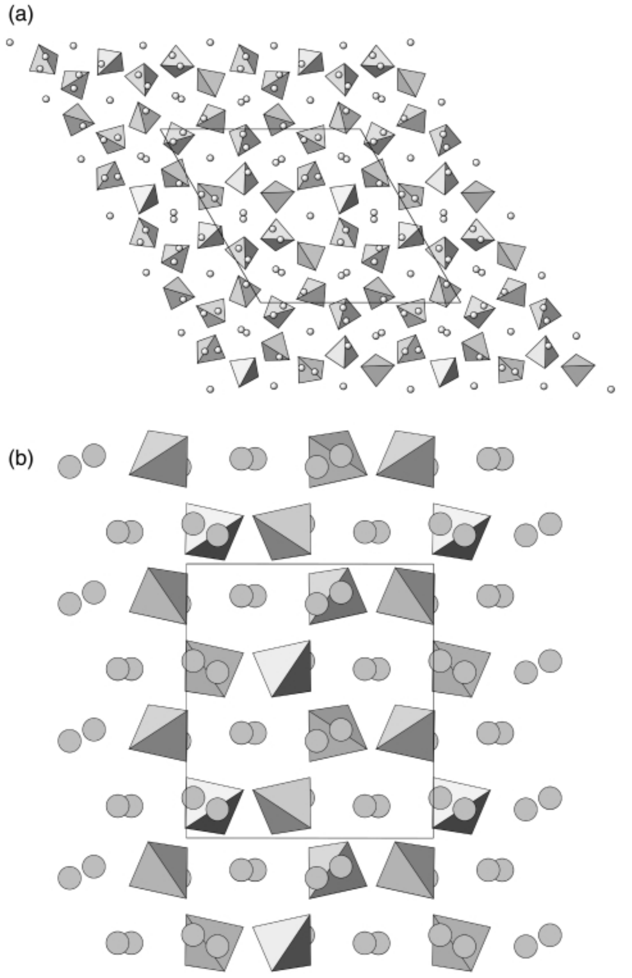

Fig. 2 (a) A [001] projection of the structure of the trigonal Ba_3MoN_4 and (b) a [010] projection of the structure of the orthorhombic Ba_3MoN_4.

tetrahedra are equally oriented with respect to the cell axes and they alternate to form regular hexagons which do not share any side or corner directly. The space between them within the unit cell is filled by four Mo2–N tetrahedra, two along the *a* axis and two along the *b* axis, which complete two more hexagons within the unit cell. These Mo1–Mo2–Mo3 hexagons are not characterised by a regular shape owing to the different orientation of the Mo2–N tetrahedra. The layers containing the hexagonal patterns, aligned along the *c* axis in trigonal Ba_3MoN_4 give raise to hexagonal channels. Ba cations are positioned within these channels. In particular, the Mo1–Mo3 hexagons are centred alternately by Ba6 and Ba8 cations: both Ba6 and Ba8 are aligned along the *c* axis. The Mo1–Mo2–Mo3 hexagons are centred alternately by pairs of Ba9 and Ba11, aligned as well along the *c* axis. Linear motifs of Mo–N tetrahedra extend along *a* and *b* in the trigonal phase and along *a* and *c* in the orthorhombic one [Fig. 3(a) and 3(b)].

In both phases Mo exhibits a four-fold coordination and N shows six-fold coordination: Ba has six-fold coordination in the orthorhombic phase and both six- and seven-fold coordination in the trigonal phase.

Mo cations form almost regular tetrahedra, whereas Ba cations form heavily distorted polyhedra with N anions, owing to the fact that Ba–N polyhedra are restricted to fit in the available sites created by the Mo–N tetrahedra framework. The Ba–N bond length ranges from *ca.* 2.6 to *ca.* 3.5 Å and the N–Ba–N angles from *ca.* 60 to *ca.* 169°. A similar range of Ba–N bonds and N–Ba–N angles is found in the orthorhombic Ba_3MoN_4 modification. Both Mo–N and Ba–N distances are similar to those found in the orthorhombic modification.[9]

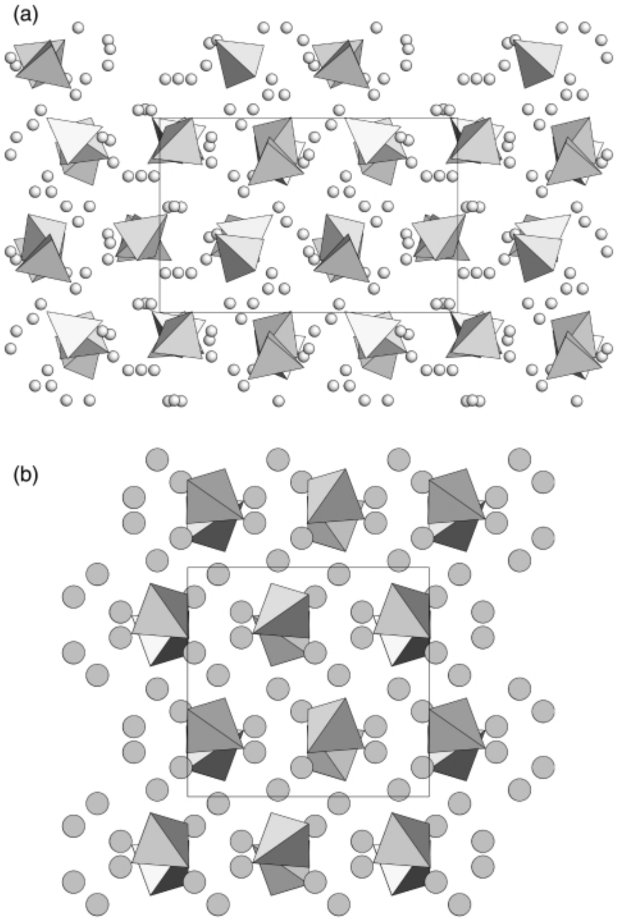

Fig. 3 (a) A [010] projection of the structure of the trigonal Ba_3MoN_4 and (b) a [001] projection of the structure of the orthorhombic Ba_3MoN_4.

Bond-valence calculations were performed for both Mo and Ba sites. The site valences of Mo are very close to the theoretical value of 6 [$v(\mathrm{Mo1}) = 6.07$, $v(\mathrm{Mo2}) = 5.895$, $v(\mathrm{Mo3}) = 6.04$] for all the Mo cations while the site valence values calculated for Ba range from 1.283 to 2.7. The same trend was found for the Ba valence sites in the orthorhombic phase [$v(\mathrm{Ba1}) = 2.438$, $v(\mathrm{Ba2}) = 1.5$, $v(\mathrm{Ba3}) = 2.5$]. These bond valence values are in contrast with those reported for most of the A_3MN_3 phases (A = Sr or Ba; M = first row transition metal) which have low alkaline-earth site valences and high transition metal site valences, and their values deviate significantly from the expected oxidation states.[6] The high transition metal site valences indicate the presence of multiple M–N bonds in the A_3MN_3 phases: the bond valence values, close to the theoretical values for Mo in nitridometalates, indicate the presence of single Mo–N bonds. This is confirmed by the Mo–N bond lengths which are comparable with those reported in the literature for alkaline and alkaline-earth ternary Mo nitrides.[2] The bond valence values may also be an indirect indication of the more ionic nature of the Mo–N bond compared to the M–N bond with M = first row transition metal. Qualitatively, the more covalent the bond, the further apart are the valence bond values from the theoretical oxidation states.[1]

The barium bond valence values stem from the wide variation in the Ba–N bond lengths and the distorted octahedral coordination round the barium atoms. This is possibly due to crystal packing effects in that the available environment for the barium atoms is dictated by the stronger bonding in the molybdenum–nitrogen tetrahedra. Tetrahedral metal coordination is very common in oxide chemistry and can therefore provide us with a link to relate the structure and properties of these two classes of chemical compounds. In particular, $M^VO_4^{3-}$ and $M^{VI}O_4^{2-}$ are isostructural and isoelectronic with the corresponding nitrides $M^VN_4^{7-}$ and $M^{VI}N_4^{6-}$. The scheelite family, with general formula ABO_4 (A = Ca, Sr, Ba, Pb; B = Mo, W) is the oxide family which shows most similarities with the Ba_3MoN_4 phases: the presence of a highly electropositive alkaline-earth metal and the transition metal in its highest oxidation state showing four-fold coordination with oxygen constitute the main structural similarities with the Ba–Mo–N compounds.[9] In both cases the Mo–X bond is affected by the so-called "inductive effect".[10] Alkaline-earth metals are strong electron donors and, therefore, render electrons available to stabilise covalency in the Mo–X (X = N, O) bond. It seems that, in the case of both nitrides and oxides, the inductive effect stabilises sp^3 hybridisation, hence the formation of Mo–X tetrahedra. Nevertheless, scheelite and trigonal Ba_3MoN_4 show different structures: ABO_4 compounds are orthorhombic with small unit cells and exhibit a different arrangement of the isolated Mo–O tetrahedra. Moreover, unlike ternary nitrides, the alkaline-earth metal forms almost regular tetrahedra with oxygen.

In conclusion, we have prepared single crystals of a trigonal phase of chemical formula Ba_3MoN_4. This proved to be a higher temperature structural modification of the orthorhombic Ba_3MoN_4 previously characterised by Gudat *et al.*[4] Trigonal Ba_3MoN_4 has a much larger cell which does not appear to be related in any way to that of orthorhombic Ba_3MoN_4. However, the two structures display several similar features such as layers of hexagonal patterns formed by isolated Mo–N tetrahedra and stacking along the shortest axis of the unit cell.

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