

## **Interstitial nitrides revisited – a simple synthesis of $M_xMo_3N$ (M = Fe, Co, Ni)**

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## **Interstitial nitrides revisited – a simple synthesis of $M_xMo_3N$ ( $M = Fe, Co, Ni$ )**

Jack O. Conway and Timothy J. Prior\*

### **Abstract**

The efficient synthesis of polycrystalline filled beta-Mn structured  $Ni_2Mo_3N$ , and the eta-carbides  $Fe_3Mo_3N$  and  $Co_3Mo_3N$ , by a single heating of metal powders at 975 °C under a hydrogen-nitrogen mixture is reported. Rietveld analysis of high-resolution X-ray powder diffraction data shows that the reduction-nitridation of  $NiMoO_4$  produces  $Ni_2Mo_3N$  and nickel;  $Ni_3Mo_3N$  is not obtained in this way and its existence is disproved.

### **Key words**

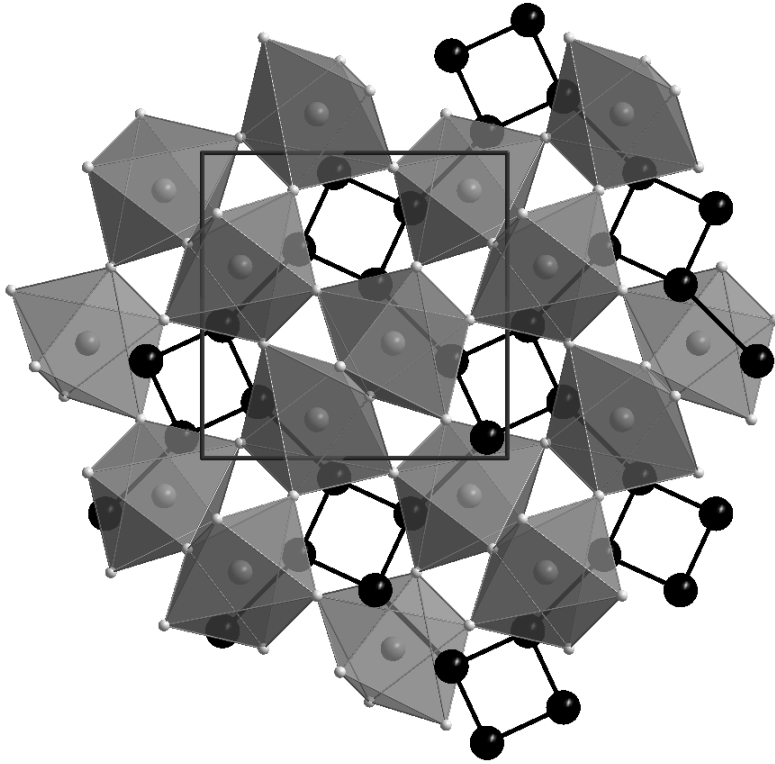
Beta manganese; eta carbide;  $Ni_3Mo_3N$ ; interstitial; catalysis; nitride

## 1. Introduction

Interstitial metal nitrides have attracted much attention due to their potential industrial applications particularly in catalysis.[1] The presence of the interstitial increases the strength of the metallic bonding and these materials often display a high toughness, making them useful as abrasives or cutting tips.[2] Some metal nitrides have a high thermal conductivity or display superconducting properties. In addition to this, many ternary nitride compounds are known to demonstrate catalytic activity, especially for the synthesis of ammonia. It has been shown that the interstitial atoms are mobile in some such phases and can be depleted and replenished.[3] Although there exist a number of different structure types which interstitial nitrides can adopt, two of the most significant are the  $\eta$ -carbide and filled  $\beta$ -manganese phases.

### 1.1. Filled $\beta$ -Manganese and $\eta$ -Carbide Structures

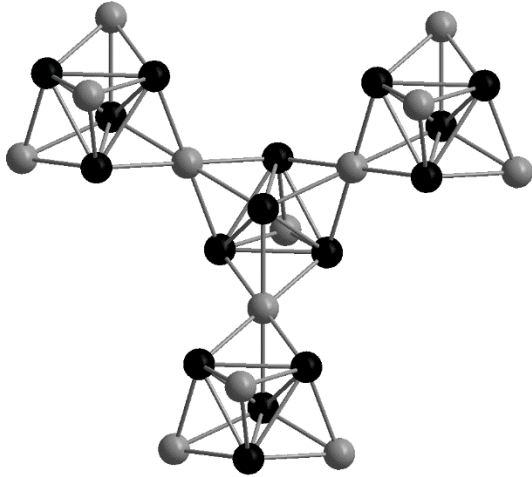
The high temperature form of manganese ( $\beta$ -Mn) is one of the most complex of any metallic element with Pearson symbol cP20. Certain interstitial compounds exist with an array of metal atoms similar to that in  $\beta$ -Mn in which there is a small non-metal atom contained within an octahedral hole; these have the *filled*  $\beta$ -Mn structure.[4] Using  $\text{Ni}_2\text{Mo}_3\text{N}$  as an example, the structure may be described in terms of two sub-units. (Figure 1) Nickel atoms are positioned on the 8c Wyckoff positions in space group  $P4_132$  (no. 213), forming a (10,3)-a network[5] of atoms. A net of corner-sharing  $\text{Mo}_6\text{N}$  octahedra fills the space within the network of nickel atoms.[6] Nitrogen atoms occupy all the octahedral holes within the structure at the 4a Wyckoff positions. The compound  $\text{Ni}_2\text{Mo}_3(\text{N/C})$  has been produced from the parent nitride and contains a random mixture of nitrogen and carbon interstitials.[7] Recently, the mineral  $\text{Pd}_3\text{Ag}_2\text{S}$ , named Coldwellite, has been reported to crystallise with the filled  $\beta$ -Mn structure.[8] Interstitial borides with the filled  $\beta$ -Mn structure have been shown to display superconductivity below 5K.[9, 10] There has been particular interest in these compounds because of the presence of magnetic order when iron or cobalt is one of the elements present.[4, 6, 11-13]



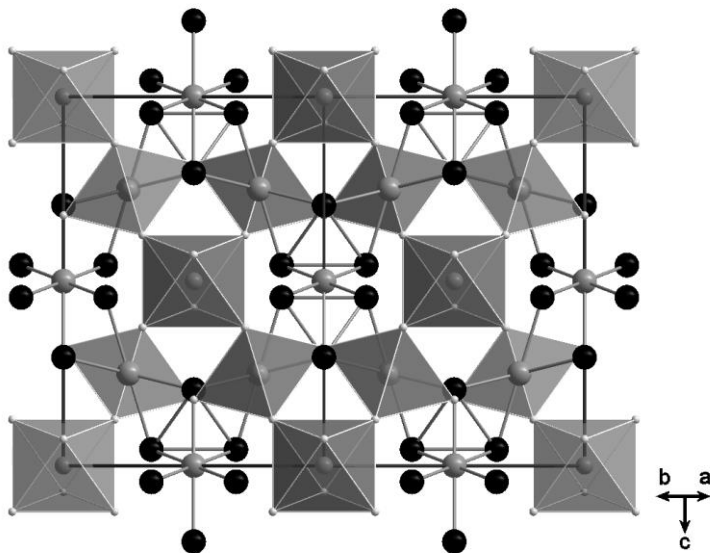
**Figure 1:** The filled  $\beta$ -Mn phase  $\text{Ni}_2\text{Mo}_3\text{N}$  viewed down 100. Nickel atoms (black) adopt a (10,3)-a network;  $\text{Mo}_6\text{N}$  octahedral (grey) occupy the space in this network.

The  $\eta$ -carbide structure is so called because of its importance as an impurity in steels.[14, 15] It may be thought of as a filled variant of the  $\text{Ti}_2\text{Ni}$  structure[16] which can be described in space group  $Fd\bar{3}m$  in terms of the Wyckoff positions of the atoms as  $\text{Ti}^{48f}\text{Ni}^{32e}\text{Ti}^{16c}$ . (Note that there are two different origins for this space group hence the Wyckoff site 16c sometimes appears as 16d.) Therefore the metal sites may be identified as  $\text{M}_3\text{M}'_2\text{M}''$ . An additional non-metal atom occupies the octahedral hole to generate an  $\eta$ -carbide  $\text{M}_3\text{M}'_2\text{M}''\text{X}$ . Various  $\eta$ -carbide nitrides such as  $\text{Fe}_2\text{W}_4\text{N}$ [17] and  $\text{Fe}_3\text{Mo}_3\text{N}$ [18] are possible depending on the occupation of the (ordered) metal sites. Using the example of  $\text{Fe}_3\text{Mo}_3\text{N}$ , the structure can be described as two diamondoid subunits. The first of these units comprises tetrahedra of metal atoms on the 32e site, in this case, iron atoms. The tetrahedra are capped over each face by the iron atoms of the 16d site, forming supertetrahedra. These supertetrahedra (sometimes referred to as *stellae quadrangulae*) share corners to form a diamondoid net. (Figure 2) The second subunit has a composition of corner-sharing  $\text{Mo}_6\text{N}$  octahedra, forming clusters which are

orientated in second diamond net. The two nets of the  $\eta$ -carbide phase are related by a translation of  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  to each other.[19] (Figure 3)



**Figure 2:**  $\eta$ -carbide structure, showing the tetrahedral formed by the atoms of the 32e site depicted in black. These are face-capped by the atoms of the 16d site, shown in grey, forming supertetrahedra.



**Figure 3:** Relationship between the two diamondoid nets of the  $\eta$ -carbide structure. The diamondoid net of corner-sharing  $\text{Mo}_6\text{N}$  octahedral fills the space in the Fe supertetrahedra net. (Colours: Fe 32e black; Fe 16d grey;  $\text{Mo}_6\text{N}$  octahedral grey)

As with the filled  $\beta$ -Mn phase, the nitrogen atoms fill the octahedral holes of the  $\eta$ -carbide structure. However, unlike the filled  $\beta$ -Mn phases, it is not essential for stability that all of octahedral holes are filled. It has been demonstrated that  $\text{Ni}_2\text{Mo}_3\text{N}$  exchanges nitrogen,[20] but no similar nitride with less nitrogen (*ie* a partially occupied interstitial site) is known. But for the  $\eta$ -carbide,  $\text{Co}_3\text{Mo}_3\text{N}$  and  $\text{Co}_3\text{Mo}_3\text{N}_{1/2}$  (normally written  $\text{Co}_6\text{Mo}_6\text{N}$ ) are known and conversion between these two phases is possible.[3] Likewise  $\text{Fe}_3\text{W}_3\text{C}$  and  $\text{Fe}_6\text{W}_6\text{C}$  can be prepared by milling of precursors and heat treatment.[21] The conversion between carbides and nitrides and their relative catalytic activity has been studied recently.[22] There has been considerable interest in the magnetic properties of nitride phases crystallising with the  $\eta$ -carbide structure and both practical and theoretical studies have been undertaken.[23-25]

## 1.2. $\text{Ni}_2\text{Mo}_3\text{N}$ and “ $\text{Ni}_3\text{Mo}_3\text{N}$ ”

Nickel molybdenum nitride,  $\text{Ni}_2\text{Mo}_3\text{N}$ , is a ternary nitride which has been shown to be an active ammonia catalyst.[20] It has been studied along with a variety of other metal nitrides in catalytic reactions. In the majority of publications, nickel molybdenum nitride has been reported as  $\text{Ni}_2\text{Mo}_3\text{N}$ , adopting the filled  $\beta$ -Mn structure type (cubic,  $a \sim 6.64 \text{ \AA}$ ).[26-32] However, there have also been a significant number of studies carried out on “ $\text{Ni}_3\text{Mo}_3\text{N}$ ”, implying that nickel molybdenum nitride adopts the  $\eta$ -carbide structure, like that of  $\text{Fe}_3\text{Mo}_3\text{N}$ . [33, 34] An early report of the Ni-Mo-N system suggested that  $\text{Ni}_3\text{Mo}_3\text{N}$  was a new orthorhombic  $\eta$ -carbide with lattice parameters,  $a = 6.635 \text{ \AA}$ ,  $b = 6.668 \text{ \AA}$ , and  $c = 6.573 \text{ \AA}$ . [35]  $\text{Ni}_2\text{Mo}_3\text{N}$  may be produced by heating stoichiometric quantities of nickel oxide and molybdenum oxide under a reducing atmosphere of dilute hydrogen in nitrogen (10%). [36]  $\text{Fe}_3\text{Mo}_3\text{N}$  can be made in a similar way or prepared by ammoniation of a 1:1 Fe:Mo oxide precursor such as  $\text{FeMoO}_4$ . It was reported that the  $\eta$ -carbide structured  $\text{Ni}_3\text{Mo}_3\text{N}$  could be produced by ammoniation of  $\text{NiMoO}_4$ . [35] This has proved controversial and doubt has been cast on the existence of  $\text{Ni}_3\text{Mo}_3\text{N}$ . [37] However, Liang *et al.* reported low resolution diffraction data that they claim show pure  $\text{Ni}_3\text{Mo}_3\text{N}$  is made in this way without the presence of nickel metal. [34]

Here we demonstrate that reports of  $\text{Ni}_3\text{Mo}_3\text{N}$  are incorrect and the ammoniation or reduction-nitridation of  $\text{NiMoO}_4$  leads to a mixture of  $\text{Ni}_2\text{Mo}_3\text{N}$  (*sic*) and nickel. Our raw data are consistent with that of Liang *et al.* but our interpretation by multi-phase Rietveld refinement

against high-resolution powder diffraction data is different and we demonstrate that  $\text{Ni}_3\text{Mo}_3\text{N}$  should be formulated as  $\text{Ni}_2\text{Mo}_3\text{N} + \text{Ni}$ . Furthermore, we also show that  $\text{Ni}_2\text{Mo}_3\text{N}$  can be made directly from the powdered metals under a hydrogen-nitrogen mixture and that this route is appropriate for the synthesis of polycrystalline  $\text{Fe}_3\text{Mo}_3\text{N}$  and  $\text{Co}_3\text{Mo}_3\text{N}$ .

## 2. Materials and methods

### *Synthesis*

The synthesis of  $\text{Ni}_2\text{Mo}_3\text{N}$  was reproduced by mixing stoichiometric amounts of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar, 98%, 13478-00-7) and  $\text{MoO}_3$  (Alfa Aesar, 99.95%, 1313-27-5). The powders were ground until homogeneous. The mixture was then fired in an electric tube furnace at 700 °C for a period of 48 hours (ramp rate 3 °C/min) under an atmosphere of dilute hydrogen (10%) in nitrogen (Energas) at a flow rate of 5 dm<sup>3</sup>/hour. The sample was reheated to 750, 850 and 950 °C, for 24 hours at each temperature, regrinding between each firing. Each firing was performed using the same reducing atmosphere, ramp rate and flow rate.

To prepare the sample of  $\text{NiMoO}_4$ , stoichiometric amounts of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar, 98%, 13478-00-7) and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  (Alfa Aesar, 12027-67-7) were mixed and ground until homogeneous. This was added to an agar solution at 90 °C made from adding 5g of agar powder to 70 ml of water, and the mixture stirred until completely homogenous. The gel was dried at 70 °C for 24 hours, before calcining at 700 °C, in air, for 3 hours, (ramp rate 5 °C/min). The  $\text{NiMoO}_4$  produced was then heated to 700 °C for a period of six hours (ramp rate 3 °C/min), under an atmosphere of dilute hydrogen (10%) in nitrogen, (flow rate of 5 dm<sup>3</sup>/hour). This was followed by a firing at 975 °C, for a period of 36 hours, under the same reducing atmosphere.

The synthesis of  $\text{Fe}_3\text{Mo}_3\text{N}$  was completed by firing a homogeneous mixture of iron powder (Hoganas Metallurgy, at least 93%, 7139-89-6) and molybdenum powder (Alfa Aesar, 99.9%, 7139-98-7) at 975 °C for 36 hours in an atmosphere of dilute hydrogen (10%) in nitrogen (flow rate of 5 dm<sup>3</sup>/hour). The metal powders were ground together by hand prior to firing to give a visible homogeneous mixture. The same procedure was followed for the synthesis of  $\text{Co}_3\text{Mo}_3\text{N}$ , using cobalt powder (Fluka, 99.8%, 7440-48-4) and for  $\text{Ni}_2\text{Mo}_3\text{N}$ , using nickel powder (Johnson Matthey, 99.9%, 7440-02-0).

We have observed no degradation of samples in air. Therefore samples were removed from the furnace after cooling to room temperature and handled in air without further special precautions.

### *Analysis*

X-ray powder diffraction data were collected using a Malvern PANalytical Empyrean powder diffractometer operating with Cu  $K\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) and a PIXcel detector. Data were collected in Bragg-Brentano geometry the range  $10 \leq 2\theta / ^\circ \leq 130$  with a step size  $\Delta 2\theta = 0.026^\circ$ . Samples were finely ground and the minimum amount of powder was mounted onto a zero-background silicon wafer sample holder.

Raw X-ray diffraction data are available. These have been uploaded to Mendeley data.

Each sample was analysed by Rietveld refinement[38] using the GSAS suite of programs[39] and the EXPGUI interface.[40] Backgrounds were fitted using a shifted Chebyshev polynomial of the first kind. Peak shapes were modelled using a pseudo-Voigt function. In all cases a zero point, lattice parameters, and atomic positions were refined. In all cases, except for  $\text{Fe}_3\text{Mo}_3\text{N}$   $U_{\text{iso}}$  values were refined where reasonable; for  $\text{Fe}_3\text{Mo}_3\text{N}$  the  $U_{\text{iso}}$  value for all atoms was set to zero.

Nitrogen analysis was performed using a Carlo Erber 1106 CHN analyser.

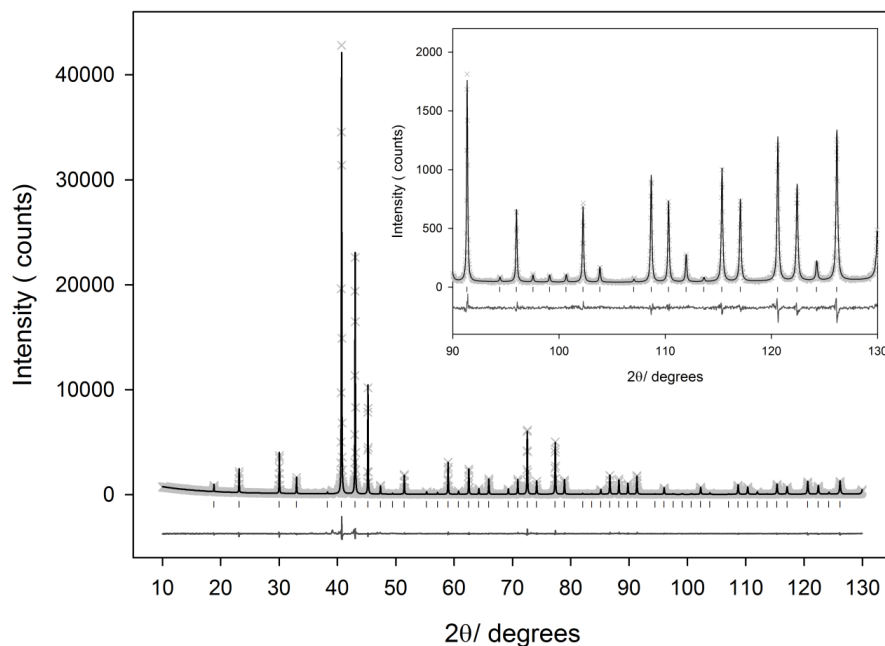
## **3. Results and Discussion**

### **3.1 Synthesis of filled $\beta$ -Mn $\text{Ni}_2\text{Mo}_3\text{N}$**

It is known that  $\text{Ni}_2\text{Mo}_3\text{N}$  can be prepared from stoichiometric mixtures of binary oxides.[36] It proved possible to repeat this using nickel nitrate hexahydrate and molybdenum oxide as the starting materials. The X-ray powder diffraction data demonstrate the single-phase nature of the product, with the diffraction pattern exhibiting the characteristic descending triplet of peaks between  $40^\circ$  and  $46^\circ 2\theta$ . To support this result, a Rietveld refinement was performed (Figure

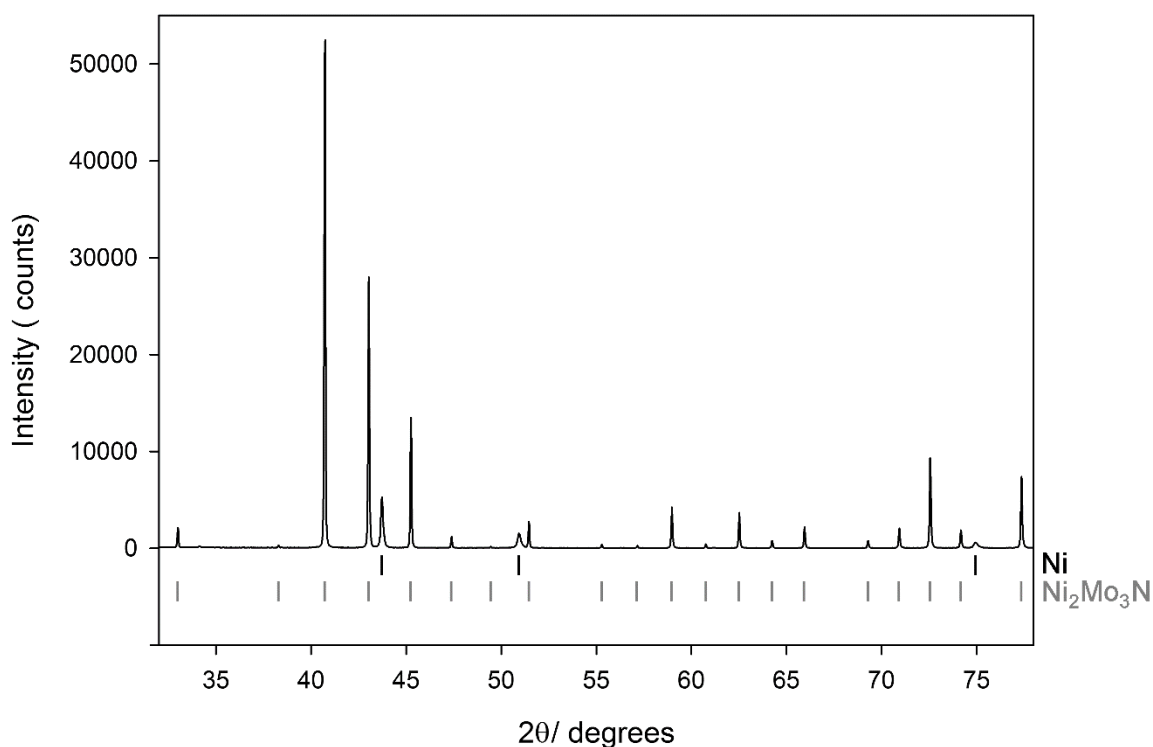


4) which displayed a good fit ( $wRp = 0.0809$ ). The structure of the product,  $Ni_2Mo_3N$  is in agreement with previous reports.[36] Details of the structure refinement are in Table 1.



**Figure 4:** Observed ( $\times$ ), calculated (line), and difference (lower line) X-ray diffraction profiles for  $Ni_2Mo_3N$  (PDF: 01-089-4564), produced from  $Ni(NO_3)_2 \cdot 6H_2O$  and  $MoO_3$ . ( $R_p = 0.0532$ ,  $wRp = 0.0809$ ). Tick marks show the positions of allowed reflections. The inset shows an enlargement of the fit in the region  $90 \leq 2\theta / ^\circ \leq 130$ .

The product of reduction-nitridation of  $NiMoO_4$  gave an X-ray powder diffraction pattern consistent with that reported by Bem *et al.*[35] and by Liang *et al.*[34] The raw data are shown in Figure 5 and the peak positions are consistent with the PDF entry number 00-049-1336 for  $Ni_3Mo_3N$ , but we can show this assignment is wrong. Similar to the data for  $Ni_2Mo_3N$  (Figure 4) the characteristic descending triplet between 40 and 46 ° 2θ is present, signifying the presence of a phase with the filled  $\beta$ -Mn structure. Extra peaks consistent with metallic nickel (43.7, 50.9, and 75.0°) are clearly indicated in Figure 5. We hope that this figure will prove useful to those working in the field of catalysis who attempt to make  $Ni_3Mo_3N$ . Rietveld refinement against the powder diffraction data in Figure 5 was carried out using a two-phase model ( $Ni_2Mo_3N$  and Ni) and provided a good fit to the data ( $wRp = 0.0867$ ) (see Table 1 and Figure S1) and unequivocally confirmed the presence of  $Ni_2Mo_3N$  (*sic*) and Ni rather than  $Ni_3Mo_3N$ . Quantitative fitting of diffraction data shows the presence of 17.5(1)% Ni in the product. We will return to the outcome of this experiment in the conclusion.



**Figure 5:** X-ray powder diffraction data from a sample of NiMoO<sub>4</sub> reduced under 10% H<sub>2</sub> in N<sub>2</sub>. The upper tick marks indicate allowed reflections for nickel (PDF: 01-077-9326) and the lower tick marks indicate allowed reflections for Ni<sub>2</sub>Mo<sub>3</sub>N (PDF: 01-089-4564).

Whilst conducting a study on the reduction of mixed metal oxides, it was observed that the reaction pathway suggested the intermediate formation of metals before the nitridation occurred. This insight suggested that it would not be necessary to utilise stoichiometric precursors or mixtures of metal oxides as starting materials. Therefore we attempted to make Ni<sub>2</sub>Mo<sub>3</sub>N and M<sub>3</sub>Mo<sub>3</sub>N (M = Fe or Co) from intimately ground mixtures of pure metals.

In line with the synthesis reported above, a highly crystalline product, Ni<sub>2</sub>Mo<sub>3</sub>N, was obtained from reduction-nitridation of mixed metal and the structure refined by the Rietveld method. An excellent fit ( $wRp = 0.0634$ ) was obtained and this demonstrated that the product was a single

phase. (See Table 1 and Figure S2) Nitrogen analysis demonstrated that the product was fully stoichiometric:  $\text{Ni}_2\text{Mo}_3\text{N}$  expected %N 3.34; observed %N 3.29.

### 3.2 Synthesis of $\eta$ -carbides $\text{M}_3\text{Mo}_3\text{N}$ (M = Fe or Co)

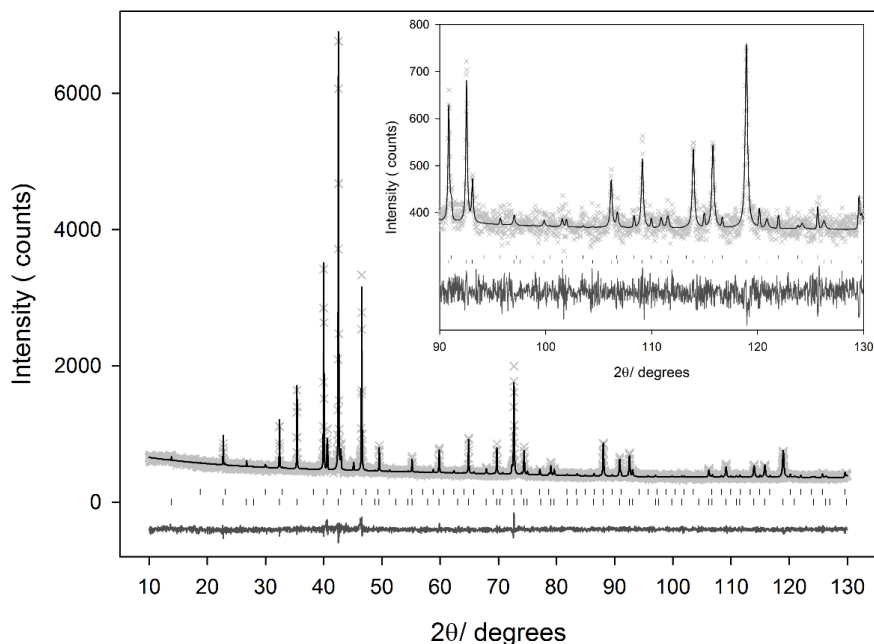
In a similar way to  $\text{Ni}_2\text{Mo}_3\text{N}$  it was possible to obtain  $\text{Fe}_3\text{Mo}_3\text{N}$  and  $\text{Co}_3\text{Mo}_3\text{N}$  directly by nitridation of mixed metal powders using 10% hydrogen in nitrogen in a one-step procedure.

#### **$\text{Fe}_3\text{Mo}_3\text{N}$**

The powder diffraction pattern showed the product to be highly crystalline and confirmed the presence of an  $\eta$ -carbide as the dominant product. Rietveld refinement confirmed the structure of  $\text{Fe}_3\text{Mo}_3\text{N}$  in line with previous reports ( $w\text{Rp} = 0.0515$ ). A small quantity of molybdenum (*ca.* 3.9(1)% by weight) was also present and this was accounted for in the data analysis. Nitrogen analysis demonstrated that the product was reasonably close to the expected stoichiometry:  $\text{Fe}_3\text{Mo}_3\text{N}$  expected %N 2.98; observed %N 2.61. Structural refinement details are contained with Table 2 and the Rietveld fit is in Figure S3. An analysis of the reported diffraction data for the much less-widely cited compound  $\text{Fe}_6\text{Mo}_7\text{N}$ [41] reveals that this is really a mixture of  $\text{Fe}_3\text{Mo}_3\text{N}$  and an iron-molybdenum alloy. (See supporting information graph S4)

#### **$\text{Co}_3\text{Mo}_3\text{N}$**

A highly crystalline product was obtained from the reduction-nitridation of a mixture of cobalt and molybdenum powders. The major product present was the  $\eta$ -carbide  $\text{Co}_3\text{Mo}_3\text{N}$ . Rietveld refinement ( $w\text{Rp} = 0.0517$ ) confirmed the structure was in good agreement with previous reports and verified that the cobalt and iron phases are isostructural.[18] Details of the refinement are contained in Table 2 and the fit is shown in Figure 6. Nitrogen analysis confirmed that the product was stoichiometric:  $\text{Co}_3\text{Mo}_3\text{N}$  expected %N 2.93; observed %N 2.87. A small amount of  $\text{Co}_2\text{Mo}_3\text{N}$  (*ca.* 7.72(18) % by weight) was also present which was allowed for in the data analysis. This is not wholly unexpected and is in line with earlier work in the Co-Mo-N system which established that  $\text{Co}_3\text{Mo}_3\text{N}$  and  $\text{Co}_2\text{Mo}_3\text{N}$  are of similar stability and one is often an impurity in the other.[36]



**Figure 6:** XRD data of the synthesis of  $\text{Co}_3\text{Mo}_3\text{N}$  using metal powders as sources of Mo and Co. Synthesised under 10%  $\text{H}_2$  in  $\text{N}_2$ . The upper tick marks indicate allowed reflections for  $\text{Co}_2\text{Mo}_3\text{N}$  (PDF: 01-072-6570) and the lower tick marks indicate allowed reflections for  $\text{Co}_3\text{Mo}_3\text{N}$  (PDF: 01-089-7953). ( $R_p = 0.0444$ ,  $wR_p = 0.0517$ ). The inset shows an enlargement of the fit in the region  $10 \leq 2\theta / ^\circ \leq 130$ .

#### 4. Discussion and conclusions

Here we have demonstrated that the composition  $\text{Ni}_3\text{Mo}_3\text{N}$  is correctly formulated as  $\text{Ni}_2\text{Mo}_3\text{N} + \text{Ni}$  and shown that the filled  $\beta$ -Mn phase  $\text{Ni}_2\text{Mo}_3\text{N}$  and the  $\eta$ -carbides  $\text{Fe}_3\text{Mo}_3\text{N}$  and  $\text{Co}_3\text{Mo}_3\text{N}$  can be formed by nitridation of the metals under hydrogen. To our knowledge this synthesis route has not been reported before.

There are recent examples of papers that report the catalytic activity of  $\text{Ni}_3\text{Mo}_3\text{N}$  obtained by ammoniation of  $\text{NiMoO}_4$ . [33, 42-47] It is notable that in contrast to other  $\eta$ -carbide nitrides, no structural refinement exists for the putative compound  $\text{Ni}_3\text{Mo}_3\text{N}$ . Some authors are adamant

that there is not nickel in their samples.[34] The data presented in the current work clearly demonstrate that reduction-nitridation or ammoniation leads to a mixture of  $\text{Ni}_2\text{Mo}_3\text{N}$  and nickel. Furthermore, we believe there is no evidence that  $\text{Ni}_3\text{Mo}_3\text{N}$  yet exists and the wide proliferation of diffraction data identified as  $\text{Ni}_3\text{Mo}_3\text{N}$  (PDF no. 00-049-1336) is an unhelpful distraction for those working on catalysis of mixed metal nitrides. We suggest it may be appropriate that powder diffraction data entries for  $\text{Ni}_3\text{Mo}_3\text{N}$  should be removed from databases.

We have a fair expectation that  $\text{Ni}_3\text{Mo}_3\text{N}$  may be discovered in the future. The existence of the  $\eta$ -carbides  $\text{Ni}_3\text{Mo}_3\text{C}$ [48] and  $\text{Ni}_3\text{W}_3\text{N}$ [37] is encouraging in this regard and many other similar Ni-containing phases have been credibly reported to adopt the  $\eta$ -carbide structure, such as  $\text{Ni}_3\text{Nb}_3\text{N}$ .[49]

There are examples of structural refinements of  $\eta$ -carbides that contain nickel such as  $\text{Ni}_2\text{GaMo}_3\text{N}$ .[50] However, electronic factors must be important here as it is possible to predict the structure of mixed-metal nitrides from a knowledge the metals present. For example,  $\text{Fe}_2\text{Mo}_3\text{N}$  is unknown but  $\text{Fe}_{1.5}\text{M}_{0.5}\text{Mo}_3\text{N}$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$  for example) adopt the filled  $\beta$ -Mn structure. Likewise  $\text{Ni}_3\text{Mo}_3\text{N}$  is unknown but  $\text{Ni}_2\text{GaMo}_3\text{N}$  is known. And as highlighted elsewhere, both  $\text{Co}_3\text{Mo}_3\text{N}$  and  $\text{Co}_2\text{Mo}_3\text{N}$  are known and it is possible to choose the desired (major) product from the synthetic method. The electronic and size factors that determine the structures are still poorly understood and this is an area in which further calculations will be valuable in the future.

The synthesis presented here is rather more efficient than that of multiple reductions of mixed metal oxides with intermittent grindings. It also removes the need for using ammonia in the synthesis. It is relatively simple to propose a straightforward mechanism for the reaction. Iron, for example, is known as a catalyst for the synthesis of ammonia from its elements; presumably at a suitable temperature ammonia is formed in the reaction and this is one of the active nitridation agents. At 1 bar pressure, under the reaction conditions, the equilibrium partial pressure of ammonia is calculated to be  $3.3 \times 10^{-3}$  bar. Finally it is notable that each of the interstitial nitrides is formed from the neutral metals under reducing conditions; oxidised metal are not needed suggesting the products are very metal-like in nature and the metal atoms have little cationic character.

These nitrides are a fertile area of research. We will be pursuing this efficient synthesis further and hope to return to it in a future publication.

## **5. Acknowledgements**

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