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Notes

Ni_2Mo_3N: A New Ternary Interstitial Nitride with a Filled *β*-Manganese Structure[†]

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Introduction

There has been much interest in the chemistry of ternary nitrides due to their unusual structures and properties.[1] Ternary and higher nitrides have not been extensively studied due to lack of a generally applicable synthesis procedure. Although Bem et al. have reported the synthesis of Ni_3Mo_3N by ammonolysis of $NiMoO_4$ at 700 °C, details of its structure and properties are not known.[2] Here we report the synthesis, structure, and properties of a new intermetallic compound, Ni_2Mo_3N.

Experimental Section

The starting material $NiMoO_4$ was prepared by the dropwise addition of an aqueous solution of $NiCl_2$ (Alfa, 98.8%) to a solution of $Na_2MoO_4{\cdot}2H_2O$ (E. Merck, 98%). The hydrated $NiMoO_4$ was filtered, washed in distilled water and ethanol, and dried at 100 °C for 12 h. A metallorganic precursor with Ni:Mo ratio 2:3 was prepared by complexing stoichiometric inorganic metal chlorides ($NiCl_2{\cdot}6H_2O$, $MoCl_5$; Fluka, 99%) in acetonitrile with triethylamine. The resulting viscous solution was hydrolyzed, and the solvent was removed by evaporation to obtain the metallorganic hydroxide precursor.[3] The title compound was synthesized by heating the precursors in flowing ammonia gas (2.5 g in an alumina boat with flow rate ∼150 mL min^{-1}) at different temperatures in a quartz tube. The sample was quenched to room temperature and the product was examined by powder X-ray diffraction (STOE-STADI/P powder X-ray diffractometer, Ge-monochromatized (fine focus setting), Cu $K\alpha_1$:$\lambda = 1.540\,56$ Å, 2θ range = 5−76°, step size = 0.02°, linear position sensitive detector) in the transmission mode. Electron diffraction patterns were obtained using a JEOL 200CX transmission electron microscope (TEM) to elucidate microstructural features. The sample was heated in oxygen atmosphere in a temperature-programmed reaction (TPR) system[4] attached to a VG QXK300 quadrupole mass spectrometer to study nitride phase formation. In a typical experiment, about 200 mg of the sample was loaded and the reactor was evacuated to 10^{-6} Torr. Oxygen gas was admitted at ca. 20−25 μmol s^{-1}, the reactor was heated from 30 to 600 °C at a rate of 15 °C min^{-1}, and the gaseous products were analyzed. Nitrogen estimation was carried out employing a home-built thermogravimetric analyzer (TGA) with heating rate 5 °C min^{-1} in O_2 atmosphere. Magnetic susceptibility of these samples was studied using a Lewis coil force magnetometer (field gradient 19 Oe cm^{-1}) and electrical properties were measured using a pressed pellet employing the four-probe technique.

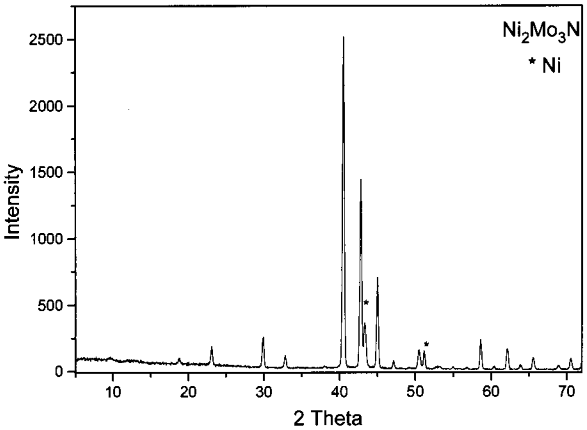

Figure 1. X-ray powder diffraction pattern of the sample heat-treated in NH_3 at 700 °C for 12 h.

Results and Discussion

Our earlier investigation on ammonolysis of $NiWO_4$ at 600 °C yielded $NiWN_2$ with metallic nickel as an impurity.[5] When $NiMoO_4$ was heated in ammonia at 700 °C for 12 h, a new phase was observed with a small amount of metallic Ni. The powder X-ray diffraction pattern of this phase is shown in Figure 1. This pattern compares well with the previously reported Ni_3Mo_3N[2,3] but not with other related known intermetallic phases such as Fe_3Mo_3N and Co_3Mo_3N.[6] The presence of nitrogen in the sample was confirmed by the detection of N_2 at 450 °C during the TPR experiment in oxygen atmosphere. Simultaneous uptake of O_2 was also observed. Because nickel phase segregation was observed during ammonolysis of nickel molybdate, the formation of a nitride phase with Ni:Mo ratio 1:1 is not likely. This suggests strongly that, even though the X-ray pattern agreed well with that reported by Bem et al., the composition might be in error. In the literature, metal-rich carbides and nitrides of the formula Ni_2Mo_3X (X = C, N) are not known. However, Ni_3Mo_3C, Ni_6Mo_6C, Co_6Mo_6C, Fe_3Mo_3N, and Co_3Mo_3N crystallizing in the η-carbide structure

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are known.[6-8] This necessitates a careful analysis of the X-ray powder diffraction pattern to gain insight into the structure of the new phase.

The X-ray powder diffraction pattern (Figure 1) obtained from ammonolysis of $NiMoO_4$ can be indexed in a cubic cell.[9] A comparison of this cell with the structure types reported in the literature[7,10] revealed that the compound prepared by us is isostructural with the Al_2Mo_3C phase.[11] The intensity pattern generated for the composition Ni_2Mo_3N using Al_2Mo_3C as the structural model displays excellent correlation with the observed intensities. The TGA of the sample was done in an oxygen atmosphere. The observed mass gain is consistent with the oxidation of a biphasic mixture, Ni_2Mo_3N and Ni to NiO and MoO_3. The chemical equations for the ammonolysis of $NiMoO_4$ and subsequent heating in an oxygen atmosphere can be given as

$$6NiMoO_4 + 16NH_3 \rightarrow 2Ni_2Mo_3N + 2Ni + 24H_2O + 7N_2 \quad (1)$$

$$2Ni_2Mo_3N + 2Ni + 12O_2 \rightarrow 6NiO + 6MoO_3 + N_2 \quad (2)$$

As there was no oxide precursor with Ni:Mo ratio 2:3, we have followed the metallorganic precursor route[3] with the required metal stoichiometry to obtain pure Ni_2Mo_3N. A single phase, Ni_2Mo_3N, was obtained by heating the chemically complexed metallorganic precursor in ammonia at 950 °C for 4 h. TPR of Ni_2Mo_3N in O_2 atmosphere did not show a CO_2 mass peak indicating the formation of a pure nitride phase. Nitrogen content was estimated by TG studies in oxygen atmosphere. The observed mass gain of 38.58% (expected: 38.63%) is consistent with the loss of N_2 along with uptake of O_2 for the oxidation of Ni_2Mo_3N to 2NiO and $3MoO_3$. The calculated molecular formula is $Ni_2Mo_3N_{1.02\pm0.02}$. A lower reaction temperature could be used for the ammonolysis of $NiMoO_4$ to obtain Ni_2Mo_3N (700 °C) as compared to the metallorganic precursor (950 °C), possibly due to the presence of small nickel particles enhancing the reaction rate.[12]

In an effort to determine the structure of this new phase unequivocally, intensity data for profile analysis were collected on an X-ray powder diffractometer. The starting model for the Rietveld refinement was derived from the Al_2Mo_3C structure.[13] Rietveld refinements were carried out using the pattern-fitting structure refinement (PFSR) package (modified version of the original Rietveld program, which is compatible with the STOE X-ray diffraction system). The thermal parameter of nitrogen was fixed at 0.06 Å^2 while all the parameters of Ni and Mo were allowed to refine freely. The occupancy refinement of Ni and Mo showed the full occupancy of these atoms at 8*c* and 12*d* sites of space group $P4_132$, respectively. Refinement converged with $R_{(I,hkl)} = 7.06\%$, $R_p = 11.07\%$, $R_{wp} = 15.90\%$, and $\chi^2 = 3.41$, and details of the refinements are given in Table 1.

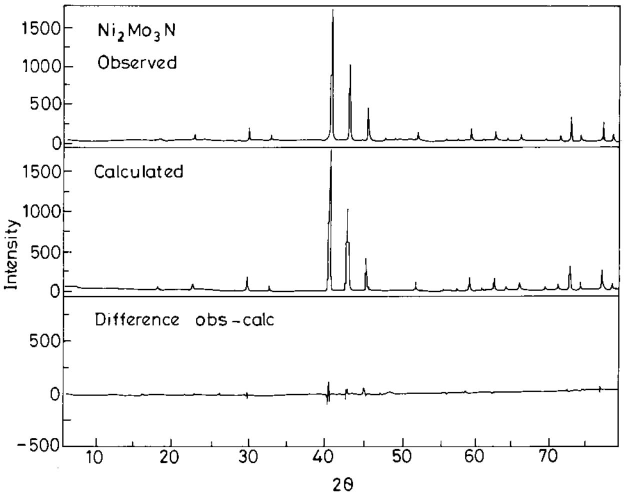

Figure 2. Observed and calculated X-ray powder diffraction pattern together with difference plot of Ni_2Mo_3N.

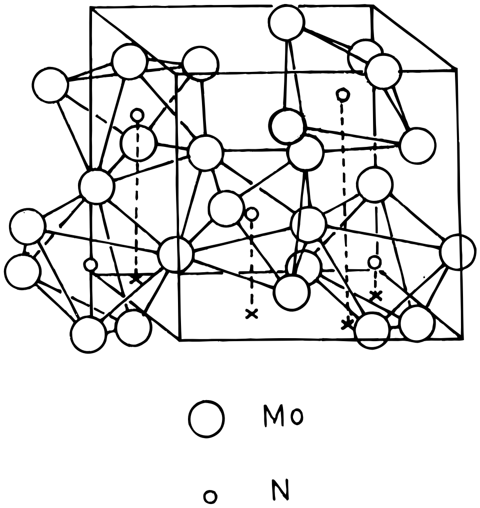

Figure 3. Unit cell of Ni_2Mo_3N emphasizing corner-shared $[NMo_6]$ distorted octahedra. The nickel atoms are not shown.

Table 1. Crystallographic Data and Structural Refinements for Ni_2Mo_3N

empirical formula	Ni_2Mo_3N
fw	419.226
crystal system	cubic
space group	$P4_132$
unit cell	6.6521(5)
volume	294.36(4)
Z	4
$F(000)$	2280.0
radiation	Cu Kα_1 (1.540 56 Å)
2θ (begin, end, step)	5,79.94,0.02
measurement time	5 s/step
refinement method	Rietveld on F^2
profile function	Pearson V11 with exponent 2.0
$R_{(I,hkl)}$/%	7.06
R_p/%	11.07
R_{wp}/%	15.90
diffraction method	transmission mode
diffractometer	STOE-STADI/P

Figure 2 shows a comparison of the experimental plot with that obtained by refinement, along with the difference plot. The refined parameters and bond distances and angles are presented in Table 2. A transmission electron microscopic study of the Ni_2Mo_3N further confirmed the structure. The selected area electron diffraction along the [001] zone axis showed the cubic

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(9) The pattern was indexed uniquely in a cubic cell ($a = 6.6515(10)$ Å) using the program REFINE (refinement of lattice constant) of the STOE-STADI/P diffraction system to a figure of merit 103.2 (defined as $F(N) = [1/[\mathrm{avg.}(2\theta)][N_{obs}/N_{pos}]]$, where N_{pos} is the number of independent diffraction lines possible up to Nth observed line).

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Table 2. Fractional Coordinates, Isotropic Temperature Factors, and Calculated Distances (Å) and Angles (deg) for Ni_2Mo_3N

atom	position	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso} (Å^2)	occupancy
Mo	12d	0.2032(5)	0.4532(5)	$^1/_8$	0.018(2)	1.0
Ni	8c	0.071(1)	0.071(1)	0.071(1)	0.025(4)	1.0
N	4a	$^3/_8$	$^3/_8$	$^3/_8$	0.06	1.0

[NMo_6] polyhedra			Ni[Ni_3 Mo_9] polyhedra			Mo[$N_2Ni_6Mo_6$] polyhedra		
N−Mo	×6	2.083(2)	Ni−Ni	×3	2.461(9)	Mo−N	×2	2.083(2)
			Ni−Mo	×3	2.718(7)	Mo−Ni	×2	2.718(7)
			Ni−Mo	×3	2.772(6)	Mo−Ni	×2	2.772(7)
Mo−N−Mo	×9	84.17(1)	Ni−Mo	×3	2.833(7)	Mo−Mo	×4	2.793(4)
Mo−N−Mo	×3	111.29(9)				Mo−Mo	×1	2.799(4)
Mo−N−Mo	×3	159.67(1)				Mo−Ni	×2	2.833(7)
						Mo−Mo	×1	3.440(1)

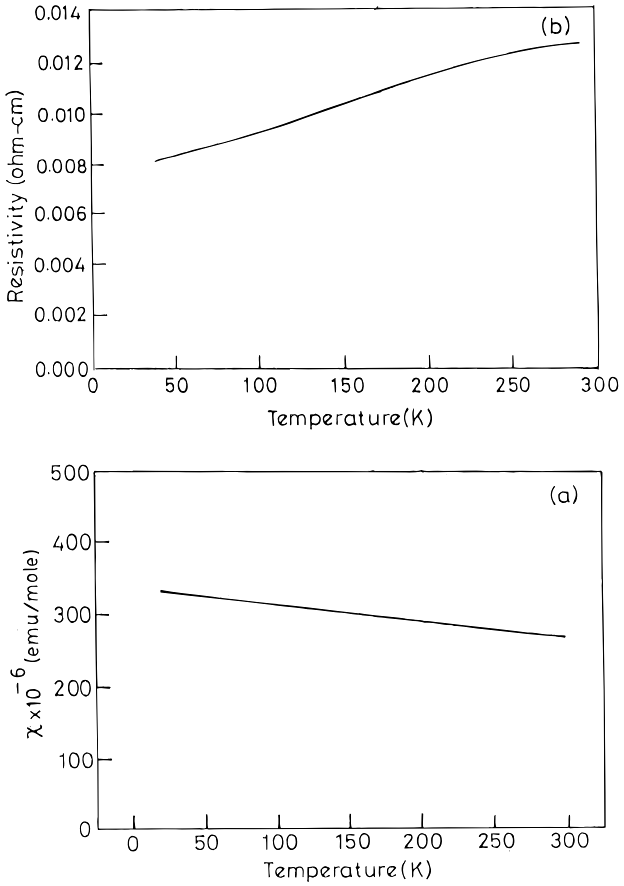

Figure 4. (a) χ vs *T* plot for Ni_2Mo_3N; (b) *R* vs *T* curve for Ni_2Mo_3N.

symmetry of the phase with a lattice parameter ≈6.7 Å, and the powder particles are in the submicron range.

The structure (Figure 3) shows corner-shared [NMo_6] octahedra in the unit cell. Nickel atoms are located in 12-fold, pseudo-icosahedral coordination, surrounded by nine molybdenum and three nickel atoms to give Ni[Mo_9Ni_3] polyhedra. The pseudo-tetradecahedron site is realized with two nitrogen, six nickel, and six molybdenum atoms to give Mo[$N_2Ni_6Mo_6$] polyhedra. In the literature of interstitial nitrides and carbides, compounds crystallizing with the β-Mn structure are very rare. It may be recalled that Ni_3Mo_3C, Fe_3Mo_3N, and Co_3Mo_3N crystallize with the η-carbide structure. While the ammonolysis of $FeMoO_4$ and $CoMoO_4$ yields isostructural Fe_3Mo_3N and Co_3Mo_3N,[6] the ammonolysis of the nickel molybdate, $NiMoO_4$, yields a new nitride, Ni_2Mo_3N, crystallizing in a filled β-Mn structure. It is important to note that, the nickel−molybdenum nitride does not crystallize in the η-carbide structure as compared to its carbide analogue. Nickel stands apart from the iron and the cobalt containing interstitial nitrides which may be due to the different sizes of the atoms and electrochemical factors.

A tungsten analogue, Ni_2W_3N ($a = 6.663(1)$ Å), isostructural with the title compound was obtained by the ammonolysis of $NiWO_4$.[14] An attempt to synthesize other members of the series with Cu, Zn, Cd, and Pb in place of nickel by the ammonolysis of $AMoO_4$ (A = Cu, Zn, Cd, Pb) precursors yielded high surface area Mo_2N and metal (A) particles.

Magnetic susceptibility measurements of the Ni_2Mo_3N showed Pauli-paramagnetic behavior (Figure 4a). The observed low magnetic moment (1.76 μ_B) is indicative of the metallic nature of the material. Resistivity measurements of the sample using a pressed pellet showed metallic behavior down to 20 K (Figure 4b). It may be recalled that Al_2Mo_3C crystallizes in a filled β-Mn structure, showing a superconducting transition at 10 K.[10] Ni_2Mo_3N did not show any such transition down to 20 K.

Conclusions

A new interstitial nitride, Ni_2Mo_3N, was synthesized and characterized for its structure and properties. This nitride belongs to a rare class of compounds crystallizing with a filled β-Mn structure and shows metallic and Pauli-paramagnetic behavior down to 20 K.

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