CHEMISTRY of MATERIALS

VOLUME 5, NUMBER 4 APRIL 1993

Communications

Synthesis of Intermetallic Nitrides by Solid-State Precursor Reduction

David S. Bem,† Charles P. Gibson,‡ and Hans-Conrad zur Loye*,†

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Department of Chemistry, University of Wisconsin
Oshkosh, Oshkosh, Wisconsin 54901

Received November 19, 1992
Revised Manuscript Received February 19, 1993

Solid-state nitrides are of interest because they exhibit technologically useful properties.[1,2] For example, some transition-metal nitrides are extremely hard and strong yet are good conductors of heat and electricity.[3-6] Others show interesting catalytic properties,[7] where the similarity between nitrides and the group VIII metals has been pointed out.[2,8,9] Because of these properties nitrides have found utility as packaging materials, as structural materials, and as catalysts. Despite the potential technological importance of nitrides, only a few hundred are known. Due to the synthetic challenges of ternary nitride formation, most studies have focused on binary nitrides.[10] We are particularly interested in the syntheses and characterization of ternary nitrides because (1) these materials may have enhanced or improved properties relative to binary nitrides and (2) relavtively few ternary nitrides have been synthesized and fully characterized.[1,2,4]

In general, nitrides have relatively low decomposition temperatures due to the high bond energy of N_2 (941 kJ/mol).[4] Consequently, high-temperature techniques have provided only limited success in the preparation of ternary nitrides and low and moderate temperature approaches become essential for preparing both metastable (kinetic) and stable (thermodynamic) compounds. The development of new low-temperature procedures for synthesizing ternary nitrides would greatly expand this class of materials. Currently there are a number of research groups working on a variety of approaches in this rapidly growing field.[11-23]

One successful approach has been the use of molecular precursors to make thin films and powders of binary

† Massachusetts Institute of Technology.
‡ University of Wisconsin, Oshkosh.
* To whom correspondence should be addressed.

(1) DiSalvo, F. J. *Science* **1990**, *247*, 649–655.
(2) Volpe, L.; Boudart, M. *J. Solid State Chem.* **1985**, *59*, 332–347.
(3) Oyama, T. S. *J. Solid State Chem.* **1992**, *96*, 442–445.
(4) Toth, L. E. *Transition Metal Carbides and Nitrides*; Academic Press: New York, 1971.
(5) Shakelford, J. F. *Introduction to Materials Science for Engineers*; Macmillan: New York, 1988.
(6) Goldschmidt, H. J. In *Interstitial Alloys*; Plenum Press: New York, 1967; pp 214–244.
(7) Kugler, E. L.; McCandlish, L. E.; Jacobson, A. J.; Chianelli, R. R. United States Patent, 5,138,111, 1992.
(8) Levy, R. B.; Boudart, M. *Science* **1973**, *181*, 547–549.
(9) Jaggers, C. H.; Michaels, J. N.; Stacy, A. M. *Chem. Mater.* **1990**, *2*, 150.
(10) Glasson, D. R.; Jayaweera, S. A. A. *J. Appl. Chem.* **1968**, *18*, 65–77.
(11) Gudat, A.; Kniep, R.; Rabenau, A.; Bronger, W.; Ruschewitz, U. *J. Less-Common Met.* **1990**, *161*, 31–36.
(12) Gudat, A.; Kniep, R.; Rabenau, A. *Thermochim. Acta* **1990**, *160*, 49–56.
(13) LaDuca, R. L.; Wolczanski, P. T. *Inorg. Chem.* **1992**, *31*, 1311–1313.
(14) Wiley, J. B.; Kaner, R. B. *Science* **1992**, *255*, 1093–1097.
(15) Zachwieja, U.; Jacobs, H. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 1055–1062.
(16) Holl, M. M. B.; Wolczanski, P. T.; Van Duyne, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 7989–7994.
(17) Gudat, A.; Haag, S.; Kniep, R.; Rabenau, A. J. *Less-Common Met.* **1990**, *159*, L29–L31.
(18) Gudat, A.; Kniep, R.; Rabenau, A. *Thermochim. Acta* **1990**, *160*, 49–56.
(19) Gudat, A.; Kniep, R.; Rabenau, A.; Bronger, W.; Ruschewitz, U. *J. Less-Common Met.* **1990**, *161*, 31–36.
(20) Gudat, A.; Kniep, R.; Rabenau, A. *Angew. Chem.* **1991**, *103*, 217–218.
(21) Höhn, P.; Kniep, R. *Z. Naturforsch.* **1992**, *47*, 477–481.
(22) Höhn, P.; Haag, S.; Milius, W.; Kniep, R. *Angew. Chem.* **1991**, *103*, 874–875.
(23) Gudat, A.; Kniep, R. *J. Alloys Compd.* **1992**, *179*, 333–338.

0897-4756/93/2805-0397$04.00/0

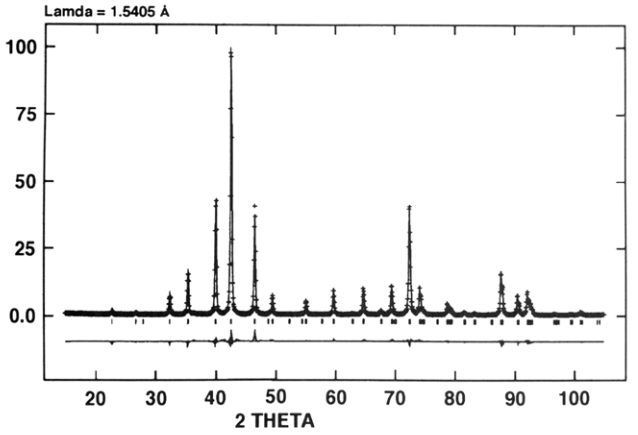

Figure 1. Powder X-ray data, including Rietveld fit and residuals, for Fe_3Mo_3N.

Table I. Atomic Positions of Fe_3Mo_3N Space Group $Fd\bar{3}m$

metal	Wyckoff	x	y	z
Mo	48(f)	0.3210	$^1/_8$	$^1/_8$
Fe(1)	32(e)	0.2937	0.2937	0.2937
Fe(2)	16(d)	$^1/_2$	$^1/_2$	$^1/_2$
N	16(c)	0	0	0

nitrides.[13,16,24] Nonmolecular precursors,[9,25] such as high surface area powders,[26] have also been used as an avenue to metastable phases. Ternary transition-metal nitrides have been synthesized by reacting a transition-metal nitride with an alkali- or alkalne-earth metal under N_2 or NH_3 yielding numerous alkali- or alkaline-earth-metal containing nitrides,[27-38] for example, $KTaN_2$,[38] Li_3FeN_2,[19] or $NaTaN_2$.[15] Another approach for synthesizing alkali-metal-containing ternary nitrides has been the use of mixed metal precursors; for example, the ternary nitride $LiMoN_2$ can be synthesized by reaction between Li_2MoO_4 and NH_3-(g).[39] We are currently investigating the use of transition-metal molybdates as precursors to ternary transition-metal nitrides, an approach that has not been extensively explored and that promises to lead to the discovery of a large number of new ternary nitrides.

In this study, transition-metal molybdates $FeMoO_4$ and $NiMoO_4$ were used as precursors for ternary transition-metal nitrides. Hydrated metal molybdates were prepared by dropwise addition of 400 mL (0.25 M) of aqueous solution of metal chloride, $FeCl_2$ (Cerac, 99.99%) and $NiCl_2$ (Cerac, 99.5%), to a 150-mL (0.55 M) solution of $Na_2MoO_4\cdot(H_2O)_2$ (Aldrich). A solid product was isolated by vacuum filtration and rinsed with two washings of water followed by a single washing with ethanol. The solid was air-dried overnight followed by a further drying at 150 °C for 24 h. The products were a brown amorphous powder ($FeMoO_4$ precursor) and a green amorphous powder ($NiMoO_4$ precursor). Calcining the amorphous products under nitrogen at 700 °C for 6 h yielded crystalline $FeMoO_4$ (JCPDS Card 16,326) and $NiMoO_4$ (JCPDS Card 33,948). The amorphous materials were used in the subsequent synthesis of Fe_3Mo_3N and Ni_3Mo_3N.

The metal molybdate precursor was placed into an alumina boat which was inserted into a quartz flow through reactor located in a hinged tube furnace. The sample was heated under flowing ammonia gas at 5 °C/min to 700 °C for M = Ni or 800 °C for M = Fe. The samples were held at the reaction temperature for 12 h and then quenched to room temperature by turning off and opening the furnace. Fe_3Mo_3N and Ni_3Mo_3N can also be prepared using forming gas (5% H_2/95% N_2) instead of ammonia

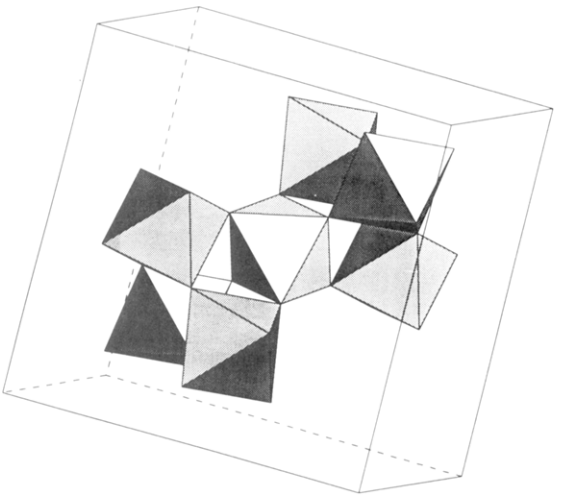

Figure 2. Corner shared NMo_6 octahedra of the Fe_3Mo_3N structure.

Table II. Indexed Powder Pattern of Fe_3Mo_3N: a = 11.083 Å

d_{obs}	d_{calc}	$h\,k\,l$	I/I_0
6.395	6.395	1 1 1	<1
3.918	3.916	2 2 0	2
3.340	3.340	3 1 1	<1
2.769	2.769	4 0 0	10
2.541	2.541	3 3 1	19
2.261	2.261	4 2 2	45
2.131	2.132	5 1 1	100
1.957	1.958	4 4 0	36
1.845	1.846	4 4 2	6
1.669	1.669	6 2 2	4
1.552	1.551	5 5 1	7
		7 1 1	
1.442	1.442	7 3 1	7
		5 5 3	
1.385	1.385	8 0 0	1
1.306	1.305	6 6 0	30
		8 2 2	
1.279	1.279	5 5 5	7
1.212	1.215	7 5 3	2
1.209	1.209	8 4 2	2
1.114	1.113	9 3 3	10
		7 7 1	

(24) Winter, C. H.; Sheridan, P. H.; Lewkebandara, T. S.; Heeg, M. J.; Proscia, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 1095–1097.
(25) Ross, C. B.; Wade, T.; Crooks, R. M. *Chem. Mater.* **1991**, *3*, 768–771.
(26) Chlorey, R. W.; Lednor, P. W. *Adv. Mater.* **1991**, *3*, 474–485.
(27) Brokamp, T.; Jacobs, H. *J. Alloys Compd.* **1991**, *176*, 47–60.
(28) Cordier, G.; Gudat, A.; Kniep, R.; Rabenau, A. *Angew. Chem.* **1989**, *101*, 1689–1690.
(29) Cordier, G.; Gudat, A.; Kniep, R.; Rabenau, A. *Angew. Chem.* **1989**, *101*, 204.
(30) Cordier, G.; Höhn, P.; Kniep, R.; Rabenau, A. *Z. Anorg. Allg. Chem.* **1990**, *591*, 58–66.
(31) Vennos, D. A.; Badding, M. E.; DiSalvo, F. J. *Inorg. Chem.* **1990**, *29*, 4059–4062.
(32) Vennos, D. A.; DiSalvo, F. J. *J. Solid State Chem.* **1991**, *98*, 318–322.
(33) Chern, M. Y.; DiSalvo, F. J. *J. Solid State Chem.* **1990**, *88*, 459–464.
(34) Chern, M. Y.; DiSalvo, F. J. *J. Solid State Chem.* **1990**, *88*, 528–533.
(35) Chern, M. Y.; Vennos, D. A.; DiSalvo, F. J. *J. Solid State Chem.* **1992**, *96*, 415–425.
(36) Juza, R.; Langer, K.; Von Benda, K. *Angew. Chem.* **1968**, *80*, 373–384.
(37) Gudat, A.; Milius, W.; Haag, S.; Kniep, R.; Rabenau, A. *J. Less-Common Met.* **1991**, *168*, 305–312.
(38) Rauch, P. E.; DiSalvo, F. *J. Solid State Chem.* **1992**, *100*, 160–165.
(39) Elder, S. H.; DiSalvo, F. J.; Doerrer, L. H. *Chem. Mater.* **1992**, *4*, 928–937.

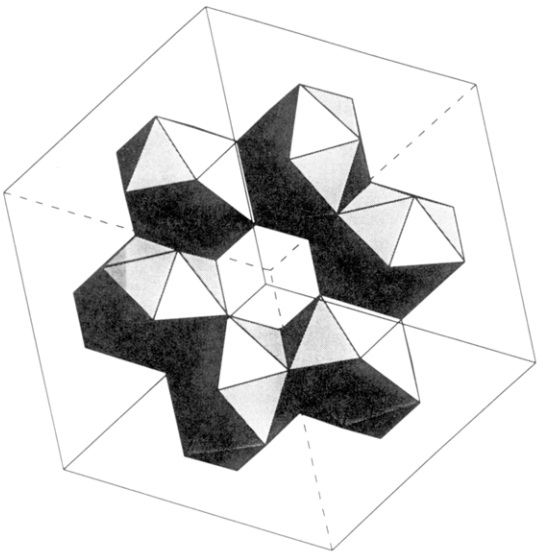

Figure 3. $Fe[Mo_6Fe_6]$ polyhedra of the Fe_3Mo_3N structure.

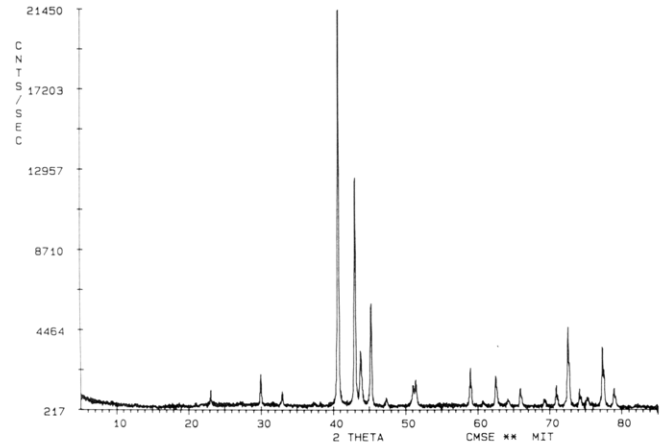

Figure 4. Powder X-ray diffraction pattern of Ni_3Mo_3N.

under the same reaction conditions. This allowed us to follow the weight loss in a TGA, which was consistent with the formation of Fe_3Mo_3N and Ni_3Mo_3N. The results of C, H, N combustion analysis (Oneida N_{Ni} = 2.81 wt %, N_{Fe} = 3.1 wt %) were in good agreement with the nitrogen content predicted from the TGA. The metal ratio for Fe_3Mo_3N was determined using EDS on a JEOL JSM 6400 scanning electron microscope collected by a Noran Z-max windowless detector with quantification performed using virtual standards on associated Voyager software. The sample was found to contain molybdenum and iron in a molar ratio of 52:47 (±3%). Observation of the nitride by SEM showed it to be a highly porous submicron (<1 μm) powder. The metal content of Ni_3Mo_3N was determined by elemental analysis (Oneida) and was found to contain a nickel to molybdenum ratio of 49:50. Further characterization of the products was carried out by X-ray powder diffraction using a Rigaku RU300 diffractometer with Cu Kα radiation (λ = 1.541 84 Å). NBS silicon was used as a standard for accurate peak positions.

Table III. Indexed Powder Pattern of Ni_3Mo_3N: a = 6.635 Å, b = 6.668 Å, c = 6.573 Å

d_{obs}	d_{calc}	$h\ k\ l$	I/I_0
3.843	3.842	1 1 1	4
2.977	2.973	2 1 0	8
2.715	2.713	2 1 1	4
2.215	2.214	1 2 2	100
2.101	2.099	3 0 1	58
2.066	2.081	1 0 3	14
2.003	2.007	3 1 1	26
1.917	1.912	2 2 2	3
1.789	1.787	2 3 1	6
1.775	1.774	3 1 2	7
1.565	1.568	0 3 3	10
1.485	1.485	4 0 2	8
1.450	1.451	4 1 2	2
1.416	1.412	2 3 3	5
1.357	1.357	4 2 2	3
1.327	1.327	5 0 0	6
1.302	1.301	5 0 1	21
1.277	1.275	3 3 3	5
1.233	1.234	4 3 2	3
1.212	1.212	5 2 1	16

The X-ray powder diffraction pattern of Fe_3Mo_3N was indexed for a cubic structure, a = 11.083 Å. The pattern is similar to that of the cubic eta carbide η-Fe_3W_3C.[40-42] Rietveld refinement in the space group $Fd\bar{3}m$ of the X-ray data resulted in the atomic positions shown in Table I with R_p = 6.6% and R_{wp} = 9.9% confirming the η-carbide structure. The data, fit, and residuals for Fe_3Mo_3N are shown in Figure 1, and the observed and calculated d spacings as well as the indexing are listed in Table II.

The structure consists of NMo_6 octahedra that are corner shared, with the iron atoms occupying the sites between the octahedra (Figure 2). The iron atoms are located in 12-fold, pseudo-icosahedral coordination, surrounded by six molybdenum and six from iron atoms, or four molybdenum, two nitrogen, and six iron atoms to give $Fe[Mo_6Fe_6]$ and $Fe[Mo_6Fe_4N_2]$ (Figure 3). Ni_3Mo_3N, unlike Fe_3Mo_3N, does not have the η-carbide structure. The X-ray powder diffraction pattern of Ni_3Mo_3N (Figure 4) is consistent with a new orthorhombic phase, a = 6.635 Å, b = 6.668 Å, and c = 6.573 Å. The observed and calculated d spacings as well as the indexing are listed in Table III.

We are currently investigating the magnetic and electronic properties of the iron and nickel molybdenum nitrides, as well as pursuing the formation of other transition metal nitrides from molybdate precursors.

Acknowledgment. Financial support from DuPont and Hoechst-Celanese is gratefully acknowledged.

(40) Kuo, K. *Acta Metall.* **1953**, *1*, 301–304.
(41) Villars, P.; Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, American Society for Metals International: Materials Park, OH, 1985.
(42) Daams, J. L. C.; Villars, P.; Vucht, J. H. N. v. *Atlas of Crystal Structure Types for Intermetallic Phases*, American Society for Metals International: Materials Park, OH, 1991.