4756 *Chem. Mater.* **2008,** *20,* 4756–4761

High-Pressure Synthesis of Superconducting Molybdenum Nitride δ-MoN by in Situ Nitridation

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Received March 20, 2008. Revised Manuscript Received May 10, 2008

Stoichiometric highly crystalline δ-MoN was obtained by in situ nitridation reaction under high pressure of 10 GPa. We developed a nitrogen source usable for in situ nitridation reaction. The high-pressure cell used in this study was composed of Mo_2N powder (layer 1) and a mixture of Mo_2N and metallic Ni powders (layer 2, the nitrogen source), where a gas-permeable separator (a thin layer of boron nitride powder) was placed between the layers. At high temperature of 1300 K, Mo_2N reacts with Ni metal in layer 2 to form less nitrogen-containing phase $MoNi_xN_y$ ($x \sim 0.5$, $y \sim 0.2$) and nitrogen, where the nitrogen moved into layer 1 and reacted with Mo_2N. X-ray diffraction, electron microprobe analysis, and magnetic measurements demonstrated the formation of stoichiometric δ-MoN with superconductive transition temperature (T_c) as high as 14 K. This in situ nitridation method using the novel nitrogen source is versatile for preparation of other nitrides under high pressure.

Introduction

Metal nitrides are materials with a variety of unique properties. A recent increasing interest in the chemical and physical properties of nitrides has accelerated studies of the binary and ternary nitrides.[1–4] The chemistry of the nitrides was significantly developed during the period between the 1930s and 1970s by a number of scientists, including Juza.[5] More recent studies have advanced our knowledge by reporting the synthesis of novel ternary nitrides containing alkaline-earth and transition-metal elements,[6,7]the unique electronic structure of alkaline-earth nitrides,[8] Li intercalation,[9,10] large crystal growth of GaN using Na flux,[11] and novel Sr-containing nitrides.[12,13] For transition-metal binary nitrides, a wide variety of physical properties have been reported.[14–29] For example, 3d transition-metal nitrides have been shown to exhibit antiferro-

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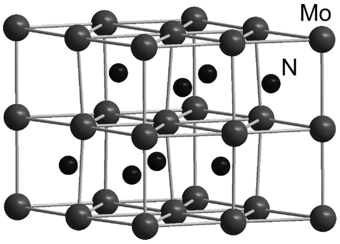

Figure 1. Crystal structure of δ-MoN.

magnetism (MnN,[14,15] CrN,[16–20] FeN[21]), Pauli paramagnetism[22] (CoN), and superconductivity[23] (TiN, VN). The discovery of the electron-doped layered hafnium nitride superconductor β-HfNCl with a transition temperature (T_c) as high as 25.5 K[30] has stimulated interest in the superconductivity of metal nitrides.

Molybdenum nitrides have attracted attention as superconducting materials. Molybdenum forms several crystalline nitrides including γ-Mo_2N (cubic), β-Mo_2N (tetragonal), and hexagonal δ-MoN.[31,32] α-Phase is known as a Mo−N solid solution with low nitrogen contents. Mo_2N crystallizes in two crystal forms: γ-Mo_2N and β-Mo_2N. γ-Mo_2N is a face-centered cubic phase with randomly distributed nitrogens in octahedral sites. β-Mo_2N is a tetragonal phase and is believed to have ordered nitrogen sites, with a doubled *c*-parameter compared to γ-Mo_2N.[32,33] γ-Mo_2N is known as a superconductor ($T_c = 5$ K),[34] and also β-Mo_2N was reported to be a superconductor ($T_c = 5.2$ K).[35] A theoretical study predicted that MoN with cubic NaCl-type structure (so-called B1-MoN) would have T_c as high as 29 K.[36] Many researchers have attempted to synthesize B1-MoN, but there is still no experimental report on B1-MoN having such a high T_c.[37]

Hexagonal δ-MoN crystallizes in an NiAs-type related ordered structure (Figure 1).[33] Early report of Matthias and Hulm described that the T_c was 12 K.[34] Later, he and his co-worker reported the phase showed T_c as high as 14.8 K when the sample was prepared in the presence of sulfur and boron under high pressure.[38] Then many reports described synthesis of δ-MoN and its superconductivity. A study reported $T_c = 15.1$ K,[39] but T_c's in other reports were distributed around 12 K, suggesting that the T_c of this compound is very sensitive to preparation conditions.[33,40,41] In general, T_c's of metal nitrides are sensitive to (1) crystallinity and (2) nitrogen stoichiometry and oxygen contamination. Crystallinity of samples can be improved by high-pressure and high-temperature treatment: Bull et al.[33] obtained well-crystallized δ-MoN by a treatment of 6 GPa and analyzed its detailed crystal structure by neutron diffraction. Their sample showed $T_c = 12$ K, which is much lower than 14.8 K. DiSalvo and his co-workers[41] prepared δ-MoN by nitridation of MoS_2 at ambient pressure and performed elemental analysis to confirm stoichiometric composition of the sample. Their sample also showed $T_c =$ 12 K, probably because the crystallinity was not very high. These studies suggested that it is not easy to obtain well-crystallized and stoichiometric δ-MoN.

Here, we report a high-pressure synthesis of δ-MoN by an in situ nitridation method. We have developed a new nitrogen source that is usable in a high-pressure cell. The cell used in this study had two layers, where one is filled with a material to be nitrided and the other is filled with the nitrogen source. This enabled the nitridation without contamination of the samples under high-pressure and high-temperature conditions. The in situ nitridation of Mo_2N under high pressure gave stoichiometric δ-MoN with a high T_c. The present study highlighted important chemistry of superconducting metal nitrides and promised a new method for their preparation.

Experimental Section

Materials. $MoCl_5$ was obtained from Aldrich Co. Ltd. Mo_2N was prepared as follows: In an Ar-filled glovebox, ca. 4 g of $MoCl_5$ was placed on an Al_2O_3 boat (ca. 5 cm × 1 cm) and the boat was set in a quartz tube. Then the quartz tube was taken out from the glove box and it was quickly started to flow dry N_2 gas in the tube without exposure of the sample to ambient atmosphere. Then the gas flow was changed to a mixture of N_2 and H_2 (5:1 in volume). The sample was heated to 1023 K under flow of the mixed gas to obtain Mo_2N. Ni powder (99.99%, < 150 μm) was purchased from Aldrich Co. Ltd. (USA).

High-Pressure Synthesis. Figure 2 shows an illustration of boron nitride (BN) cell used in the high-pressure syntheses in this study. The cell was composed of two thick layers (layer 1 and layer 2) and a separator. In layer 1, Mo_2N powder was placed as the starting material of δ-MoN. Layer 2 was filled with a reaction mixture that produced nitrogen at high temperature (nitrogen source). As the separator, we used BN powder, which was prepared by pulverization of bulk h-BN chunks with a file.

At first, we used a mixture of NaN_3 powder and Au beads as the nitrogen source, expecting the following reaction:

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$$NaN_3 + 2Au \rightarrow Au_2Na + (3/2)N_2 \qquad (1)$$

In this case, 0.0803 g of NaN_3 and 0.536 g of Au beads were filled in layer 2 of the high-pressure cell. This sample was denoted by sample 1.

Next, we used a mixture of Mo_2N and Ni powder as the nitrogen source. Mo/Ni molar ratio in the mixture was 0.924, and (Mo in layer 1)/(Mo in layer 2) molar ratio was 0.123. This sample was denoted by sample 2.

The cell assembly for the high-pressure synthesis was described elsewhere.[42] The BN cell was surrounded by a Ta-tube heater. Then the cell with the heater was set in an MgO octahedron with an edge length of 13 mm. A K-type thermocouple was put at the side of the Ta heater. High-pressure and high-temperature experiments were carried out using Kawai-type multianvils. The octahedron was placed in the center of eight truncated tungsten carbide cubes as anvils (truncation edge length: 8 mm) and compressed in the multianvil apparatus up to 10 GPa, followed by heating to temperatures of 1300 K in 10 min. After keeping the samples at the temperature for 1 h, they were cooled down to room temperature. Then the pressure was gradually released.

Characterization. Powder X-ray diffraction patterns were measured with a BRUKER AXS, D8 ADVANCE using nickel-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). The composition was determined on an electron probe microanalyzer (EPMA) (JEOL, JCMA-733 II). Molybdenum, nickel, oxygen, nitrogen, gold, and sodium were analyzed quantitatively using molybdenum metal, nickel metal, MgO, GaN, Au, and $NaAlSi_2O_6$ as standard samples. Magnetic susceptibility was measured using a MPMS-5S magnetometer (Quantum Design) at 2− 30 K and at 15 Oe.

Results and Discussion

Sodium Azide (NaN_3) and Au Mixture as the Nitrogen Source. First, we tried to use a mixture of NaN_3 and Au as a nitrogen source (sample 1). NaN_3 decomposes at ca. 600 K to produce Na and N_2. Au beads were used to prevent the Na diffusing from layer 2 into layer 1 because it is known that Na and Au form the alloy Au_2Na. The cell was heated to 1300 K for 1 h under 10 GPa. Figure 3 shows a powder X-ray diffraction pattern of the sample of layer 1 (Figure 3a) and the starting material Mo_2N (Figure 3b). The starting material was almost pure β-Mo_2N. It is known that β-Mo_2N readily transforms into γ-Mo_2N at ca. 1100 K.[31] It is notable that δ-MoN was formed in layer 1, indicating that nitrogen from the nitrogen source (layer 2) reacted with Mo_2N in layer 1. However, γ-Mo_2N was still observed in the diffraction pattern. Furthermore, weak diffraction peaks due to Au_2Na and Au were observed as well as unknown peaks, indicating that these components diffused from layer 2 to layer 1. The melting points of Au_2N and Au are 1263 and 1336 K, respectively. In the high-pressure high-temperature conditions, the alloy might melt and could readily diffuse through the BN powder separator to contaminate the sample. It was difficult to estimate the phase fraction in layer 1 from the powder X-ray diffraction because many peaks overlapped with each other.

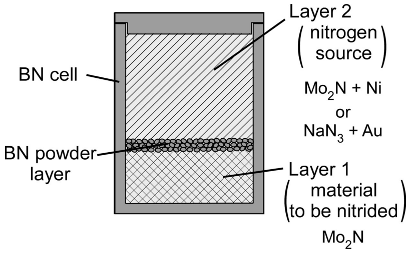

Figure 2. High-pressure cell for in situ nitridaion.

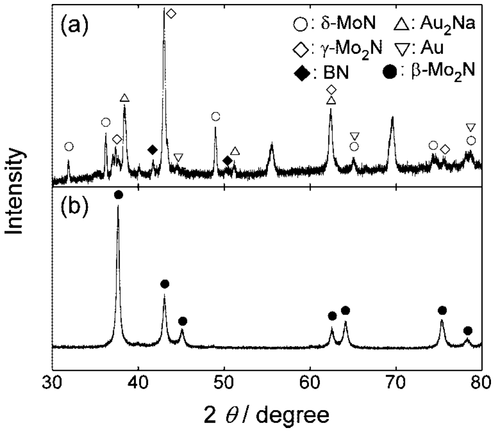

Figure 3. Powder X-ray diffraction patterns of sample 1 (layer 1) prepared by using a mixture of NaN_3 and Au beads as a nitrogen source (a), and the source material (Mo_2N) (b).

Table 1 lists composition and cell parameters of the phases observed in this study. The composition was determined by EPMA analyses. The composition of δ-MoN in sample 1 was determined to be $Mo_1N_{0.97}O_{0.13}$.

Figure 4 shows temperature dependence of magnetic susceptibility for layer 1 of sample 1. Two clear transitions in the zero-field cooling curve indicated the presence of superconductors with T_c of 12.0 and 4.2 K, which correspond to δ-MoN and γ-Mo_2N observed in the powder X-ray diffraction. The data in Figure 4 indicate that the amount of δ-MoN was much larger than that of γ-Mo_2N in layer 1.

Reaction of Mo_2N and Ni as a Nitrogen Source (Layer 2). Next, we tried to use a mixture of Mo_2N and Ni as the nitrogen source in layer 2. Figure 5 shows powder X-ray diffraction of layers 1 and 2 for this sample (sample 2). After the high-pressure and high-temperature treatment (10 GPa, 1300 K), new diffraction peaks appeared in the X-ray diffraction pattern of the nitrogen source layer 2 (Figure 5b). These peaks are assigned to Mo_3Ni_3N reported in the literature.[43] The crystal structure of this compound is unknown. Besides the peaks of this phase, diffraction peaks of δ-MoN and γ-Mo_2N were also observed.

Figure 6 shows secondary electron images (taken with EPMA apparatus) of sample 2. As shown in Figure 6, in layer 2, Ni reacted with Mo_2N to form Ni−Mo−N ternary nitride. EPMA analysis gave composition of this phase as $MoNi_{0.54}N_{0.21}O_{0.03}$ (Figure 6b and Table 1). It is notable that this phase contains a lower amount of nitrogen: The N/Mo atomic ratio was less than 0.5. That is, Mo_2N reacted with

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Table 1. Compositions and Lattice Parameters of the Samples Prepared in This Study

sample	no.[a]	composition[b]	phase[c]	cell parameter[c] (nm)		V (nm^3)
				a	c	
sample 1 (layer 1)		Mo$_1$N$_{0.97}$O$_{0.13}$Na$_{0.03}$	δ-MoN	0.5728(2)	0.5621(3)	0.1597(1)
		Mo$_1$N$_{0.58}$O$_{0.11}$Na$_{0.02}$	γ-Mo$_2$N	0.419(1)		0.0737(7)
sample 2 (layer 1)	1	Mo$_1$N$_{1.02}$O$_{0.04}$Ni$_{0.00}$	δ-MoN	0.57298(9)	0.5621(1)	0.15982(5)
	2	Mo$_1$N$_{1.04}$O$_{0.04}$Ni$_{0.00}$				
	3	Mo$_1$N$_{0.52}$O$_{0.07}$Ni$_{0.00}$	γ-Mo$_2$N	0.4165(2)		0.0723(1)
sample 2 (layer 2)	4	Mo$_1$N$_{0.21}$O$_{0.03}$Ni$_{0.54}$	Ni$_3$Mo$_3$N			
	5	Mo$_{0.07}$N$_{0.00}$O$_{0.01}$Ni$_1$	Ni			
	6	Mo$_1$N$_{0.68}$O$_{0.08}$Ni$_{0.00}$	γ-Mo$_2$N	0.4180(2)		0.0731(1)
	7	Mo$_1$N$_{0.93}$O$_{0.13}$Ni$_{0.00}$	δ-MoN	0.5730(2)	0.5662(3)	0.1599(1)
			δ-MoN[d]	0.5725	0.5608	0.1591
			γ-Mo$_2$N[e]	0.4163		0.0721

[a] No. of analyzed points shown in Figure 6. [b] Analyzed by EPMA. [c] Analyzed by powder X-ray diffraction. [d] PDF No. 25-1367. [e] PDF No. 25-1366.

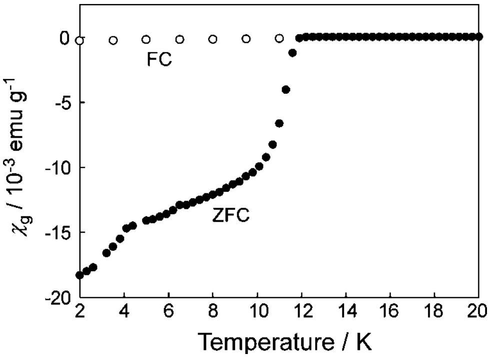

Figure 4. Magnetic susceptibility of sample 1 (layer 1). FC and ZFC represent field cooling and zero-field cooling, respectively.

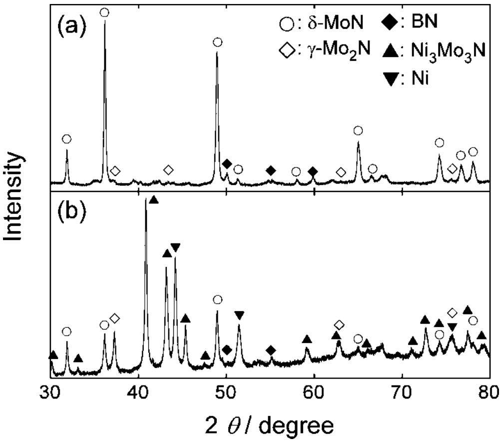

Figure 5. Powder X-ray diffraction patterns of sample 2 prepared by using a mixture of Mo$_2$N and Ni as a nitrogen source: (a) Layer 1; (b) layer 2.

Ni to produce nitrogen as well as this ternary nitride. The reaction is as follows:

$$Mo_2N + 2xNi \rightarrow 2MoNi_xN_y + [(1-2y)/2]N_2 \qquad (2)$$

In Figure 6b, the areas of Mo−Ni−N ternary phase (white parts, point no. 4) were located between those of Mo−Ni alloy (the darkest gray, point no. 5) and residual molybdenum nitrides (light gray, point nos. 6 and 7). This configuration is consistent with the above reaction. In the areas of the molybdenum nitrides, the parts close to the border with the Mo−Ni−N ternary phase (point no. 7) looked darker compared to the central parts (point no. 6). This is due to the difference in the nitrogen contents. As shown in Table 1, the border parts (no. 7) have composition close to MoN, being consistent with the presence of δ-MoN in the powder X-ray diffraction (Figure 5b). The presence of δ-MoN indicated that a part of nitrogen generated in layer 2 reacted with residual molybdenum nitride.

Figure 7 shows temperature dependence of magnetic susceptibility of sample 2. The data for layer 2 (Figure 7b) demonstrated the presence of superconductor with $T_c = 14.0$ K, which is attributable to δ-MoN.

Structure, Composition, and Superconductivity of δ-MoN (Layer 1) Prepared by Using the Mo$_2$N and Ni as a Nitrogen Source. Figure 5a shows the powder X-ray diffraction pattern of the sample in layer 1. Very sharp peaks of δ-MoN were observed. Diffraction peaks of γ-Mo$_2$N are very weak. Figure 6b shows the secondary electron image taken with an EPMA apparatus of layer 1. A large amount of δ-MoN was observed besides γ-Mo$_2$N. This indicated that in situ nitridation reaction occurred in layer 1. It is notable that no Ni was detected in layer 1, demonstrating the successful in situ nitridation by using the double-layer high-pressure cell. It should be noted that, as shown in Table 1, the stoichiometric δ-MoN was formed in layer 1.

The temperature dependence of magnetic susceptibility for this sample was shown in Figure 7a. The data indicated superconductivity with a transition temperature (T_c) as high as 14.0 K. The fraction of superconductivity was high (more than 100% calculated from the diamagnetism at 2 K), demonstrating that the superconductivity was ascribed to the main part of the sample. EPMA detected residual γ-Mo$_2$N and MoN. However, powder X-ray diffraction and the magnetic data did not show the presence of γ-Mo$_2$N ($T_c \sim 5$ K). The specimens for EPMA were prepared by polishing the samples buried in resins to observe intersection of the samples. If the γ-Mo$_2$N phases are surrounded by δ-MoN phases, it is possible that X-ray diffraction and magnetic measurement do not detect γ-Mo$_2$N, where EPMA detects γ-Mo$_2$N. Consequently, the superconductivity with $T_c = 14.0$ K was attributed to the stoichiometric δ-MoN.

Superconductivity of δ-MoN Prepared in This Study in Comparison with Those in the Literature. In the literature, δ-MoN has been studied by many researchers and

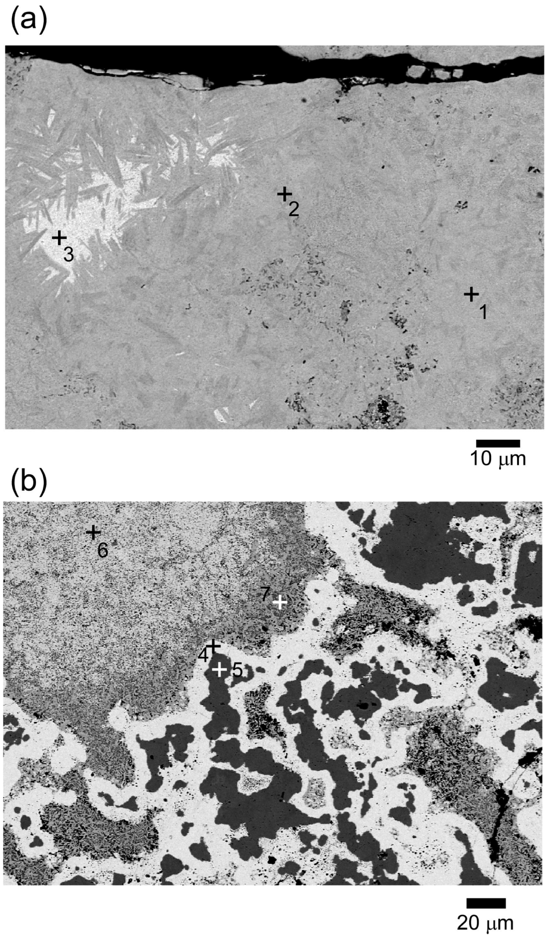

Figure 6. SEM image of sample 2 analyzed by EPMA: (a) Layer 1; (b) layer 2. The crosses represent the analyzed points.

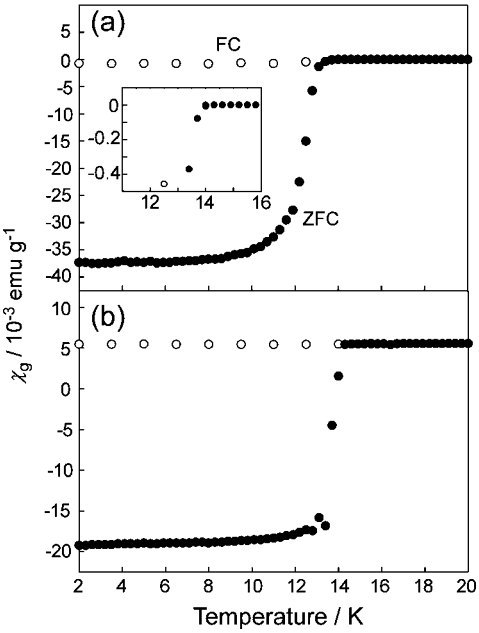

Figure 7. Magnetic susceptibility of sample 2: (a) Layer 1; (b) layer 2. The inset shows magnified plots of the data for layer 1.

is reported to be a superconductor. However, the reported transition temperatures of this phase are considerably different in the literature. In the earliest report Mathias and Hulm described that MoN had T_c of 12 K.[34] Later, they reported a high-pressure preparation of δ-MoN in the presence of sulfur and boron.[38] The obtained δ-MoN had T_c as high as 14.8 K. Bezinge et al. reported δ-MoN with T_c = 15.1 K treated under high pressure, but they also described at the same time that T_c's of δ-MoN were sensitive to the treatment conditions and changed widely from 11.0 to 15.1 K.[39] Most of theT_c's reported in the literature were around 12 K.[33,40,41] Furthermore, most of these studies did not perform elemental analysis of the prepared samples. On the other hand, Marchand et al.[41] prepared δ-MoN by ammonolysis reaction from MoS_2 and characterized the products carefully. They carried out elemental analysis of nitrogen and oxygen and found that their sample had an almost stoichiometric (or slightly excess) amount of nitrogen and a small amount of oxygen. The T_c of their sample was 12 K. Bull et al. reported high-pressure synthesis of well-ordered δ-MoN and analyzed carefully the crystal structure by neutron diffraction.[33] Their sample showed T_c of 12.1 K. They did not report elemental analysis of their sample.

Considering these reports in the literature, we noted that no report carried out both high-pressure synthesis and elemental analysis to confirm the formation of well-crystallized and stoichiometric δ-MoN. We supposed that nitridation under high pressure is indispensable for obtaining the stoichiometric nitride because many metal nitrides tend to release their nitrogen at high temperature: [44] For instance, CrN decomposes to Cr_2N at high temperature. Kawashima et al. described very briefly that high-pressure and high-temperature treatment of a mixture of γ-Mo_2N and NaN_3 resulted in T_c = 13.2 K,[45] but the use of NaN_3 brings about a contamination of samples with Na. As was described above, we tried to use NaN_3 and Au because Au "absorbs" Na formed by decomposition of NaN_3, but the Au_2Na alloy diffused into the sample layer to contaminate it.

Our method using newly developed nitrogen source (Mo_2N and Ni mixture) and double-layered high-pressure cell worked well for this preparation. Consequently, the in situ nitridation under high pressure was successfully done to obtain well-crystallized δ-MoN with stoichiometric composition. As a result, the sample showed T_c as high as 14.0 K. The nitride contained only a small amount of oxygen. Considering the present results, the conditions needed for high T_c are (1) well-crystallized (well-ordered) sample prepared under high pressure, (2) stoichiometric nitrogen content, which were achieved by in situ nitridation in this study, and (3) little oxygen contamination.

Versatility of in Situ Nitridation and the Novel Nitrogen Source for High-Pressure Synthesis of Metal Nitrides. In this study we developed a novel nitrogen source: a mixture of Mo_2N and Ni. This nitrogen source worked well for the in situ nitridation. The Ni did not contaminate the sample (in layer 1). The in situ production of nitrogen may have some effect to prevent oxygen from penetrating from the outside into the cell. Mo is a metal with a high melting point so that Mo is not likely to contaminate the sample

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(44) Pierson, O. N. *Handbook of Refractory Carbides and Nitrides. Properties, Characteristics, Processing and Applications*; Noyes Publications: Park Ridge, NJ, 1996.

(45) Kawashima, T.; Takayama-Muromachi, E.; McMillan, P. F. *Physica C* **2007**, *460*−*462*, 651–652.

through the separator. The nitrogen source may be thereby widely versatile for preparation of many other metal nitrides by in situ nitridation. Preparation of various metal nitrides by this in situ nitridation is an interesting subject for future studies.

Conclusions

We developed a novel method for in situ nitridation in a high-pressure cell. A mixture of Mo_2N and Ni was found to work well as a nitrogen source. This method was applied to the synthesis of δ-MoN using a double-layer high-pressure cell. The sample obtained at 10 GPa and at 1300 K showed superconductivity with a T_c as high as 14.0 K, which was attributed to the formation of well-crystallized and stoichiometric δ-MoN.

Acknowledgment. This work was partially supported by a Grant-in-Aid on Priority Areas (No. 436 and 472) from the Japan Ministry of Education for Science, Culture, Sports and Technology (MEXT), and by a Grant-in-Aid for Scientific Research (S) and (B), and that for Exploratory Research from the Japan Society for Promotion of Science (JSPS).

CM800820D