Review article

Recent advance in high-pressure solid-state metathesis reactions

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Abstract

High-pressure solid-state metathesis (HPSSM) reaction is an effective route to novel metal nitrides. A recent advance in HPSSM reactions is presented for a number of examples, including 3d transition metal nitrides (ε-Fe$_3$N, ε-Fe$_{3-x}$Co$_x$N, CrN, and Co$_4$N$_x$), 4d transition metal nitrides (MoN$_x$), and 5d transition metal nitrides (Re$_3$N, WN$_x$). Thermodynamic investigations based on density functional theory (DFT) calculations on several typical HPSSM reactions between metal oxides and boron nitride indicate that the pressure could reduce the reaction enthalpy ΔH. High-pressure confining environment thermodynamically favors an ion-exchange process between metal atom and boron atom, and successfully results in the formation of well-crystalized metal nitrides with potential applications.
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1. Introduction

The vast majority of the materials available in nature contain oxygen in the forms of oxides, silicates, and carbonates. The appearance of nitrides, however, is quite rare in nature. Oxides exceed nitrides in number by more than two orders of magnitude due to higher reactivity of oxygen with respect to nitrogen. There has been considerable interest in the synthesis of new metal nitrides due to their potential technological and fundamental importance. The preparation of high-quality metal nitrides, however, is a challenge because the incorporation of nitrogen into a metal lattice is thermodynamically unfavorable under atmospheric pressure. Decomposition and nitrogen-deficient problems are often encountered in the conventional metal nitrides synthetic route, in which metal nitrides are prepared by the reaction of metal or metal oxides with gaseous ammonia and hydrazine. Alternatively, high-pressure synthesis reaction and solid-state metathesis reaction provide effective routes to metal nitrides.

1.1. High-pressure synthesis (HPS) reaction

A high-pressure confining environment allows nitrogen to participate in chemical reaction unhindered by the competition from oxygen. High-pressure synthesis of metal nitride has traditionally involved synthesis reactions between elemental metal and nitrogen as given in Eq. (1)

$$M \text{ (metal)} + x N_2 \rightarrow MN_x. \tag{1}$$

Over the past few decades, this simple approach has resulted in a wide variety of novel metal nitrides including noble metal nitrides (PtN$_2$ [1], IrN$_2$ [2], and OsN$_2$ [3]), Th$_3$P$_4$-type metal nitrides (Zr$_3$N$_4$ [4] and Hf$_3$N$_4$ [5]), and 5d transition metal nitrides (Re$_3$N and Re$_2$N [6]). Performing HPS reaction between metal elements and nitrogen by means of laser heating diamond anvil cell (LHDAC) technology can

effectively prevent the thermal decomposition and volatility of reagents and products. However, the common drawbacks of this method include micrometer-scale sample size, poor crystallinity, and nonstoichiometric product formation.

1.2. Solid-state metathesis (SSM) reactions

Traditionally, reactions in which both precursors exchange components to each other are called double-displacement or double-decomposition (metathesis) reactions. This reaction is represented by the general scheme:

$$P-X + Q-Y \rightarrow P-Y + Q-X. \tag{2}$$
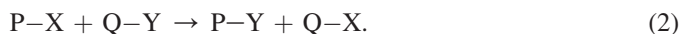
The solid-state metathesis (SSM) reaction, discovered in the 1990s and extensively investigated by the groups of Kaner [7], Parkin [8], and Chen [9], has been developed as an effective route to many refractory materials in the fields of metal borides, nitrides, and carbides. The SSM reaction for synthesis of a metal nitride typically involves a solid-state metal halide and a solid-state alkaline or alkaline-earth nitride compound. A typical SSM reaction between GaI_3 and Li_3N produces GaN as given in Eq. (3) [10]:

$$GaI_3 + Li_3N \rightarrow GaN + 3LiI. \tag{3}$$

The uncontrollable combustion-like SSM reaction ignites at a certain temperature and quickly propagates without continuous external heating because it has very low activation energy (E_a). The SSM reaction is driven by salt formation with very high reaction enthalpy (ΔH). The typical byproducts of SSM synthetic routes are often poorly crystalline and have limited scalability as a consequence of the very short reaction time (typically less than a few seconds). Previous studies also show that crystalline phase GaN is inaccessible when initiated from ambient conditions, but can be synthesized by initiating the SSM reaction under pressure [10].

2. High-pressure solid-state metathesis (HPSSM) routes

2.1. Initial discovery and general chemical reaction

A high-pressure solid-state metathesis (HPSSM) route with novel reaction precursors was first reported in 2009 by Lei and He on the synthesis of GaN [11]. The first HPSSM reaction between ternary mixed metal oxides $LiGaO_2$ and BN produces GaN crystals as given as follows,

$$LiGaO_2 + BN \rightarrow GaN + LiBO_2. \tag{4}$$

It shows that $LiGaO_2$ reacts with BN to produce GaN and $LiBO_2$. This reaction only occurs at high pressure and high temperature. The GaN products of HPSSM synthetic routes have larger crystallite size and better crystallinity as compared with the conventional SSM synthetic routes [9,11]. The original finding reveals that pressure can open an unexpected ion-

exchanged pathway for a synthesis reaction under high pressure. Over the past eight years, the laboratory has reported on HPSSM reactions between diverse metal oxides and BN that form well-crystalline Fe_3N [12], Re_3N [13], VN [14], CrN [15], W_2N_3 [16], MoN_2 [17] and other binary metal nitrides, in addition to successful syntheses of ternary metal nitride alloys, such as $Fe_{3-x}Co_xN$ and $Fe_{3-x}Ni_xN$ [18].

The HPSSM reaction experiments were performed on a DS 6×14 MN (or DS 6×8 MN) cubic press installed at Sichuan University, China. Before high-pressure and high-temperature experiments, the reaction precursors were mixed in the optimized molar ratio and placed in a capsule made of graphite or platinum which was used to seal and heat the samples in the synthesis experiments, then contained in a high-pressure cell. This cell assembly was put into a high pressure chamber. The samples were first pressurized to a certain pressure, then heated to a desired temperature. The details were described elsewhere [11,13,19].

Table 1 lists the recent advance in HPSSM reactions between boron nitride and metal oxides. The general equation for these HPSSM reactions can be depicted in Eq. (5) [19].

$$A_xM_yO_z + (2z-ax)/3\ BN \rightarrow y/w\ M_wN + 0.5[(2z-ax)/3 - y/w]\ N_2 + A_xB_{(2z-ax)/3}O_z, \tag{5}$$
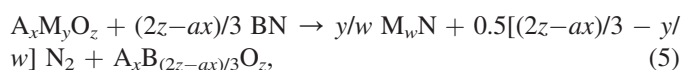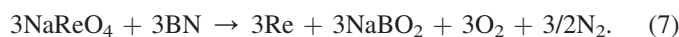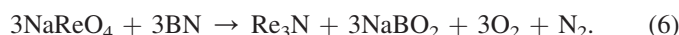
where $a = 1$ when A is an alkaline metal, and $a = 2$ when A is an alkaline-earth metal; $x = 0$ when metal oxide precursor is binary, and $x \neq 0$ when the precursor is ternary. Metal A indicates the alkaline metal (Li, Na, K) or alkaline-earth metal (Mg, Ca), and metal M represents main group or transition metal (Ga, In, Fe, V, Cr, W, Mo, Re, etc). Fig. 1 summarizes the elements involved in HPSSM reactions. The striking feature of the HPSSM routes is that they are based on a solid-state precursor reaction which proceeds via an ion exchange between B and M metal, in which pressure plays an essential role in the reaction process. It can be expected that much more important materials could be synthesized through the proposed HPSSM reaction in the near future.

2.2. Reaction characteristics

HPSSM reaction routes could provide advantages over conventional SSM synthetic methods because of high-pressure confinement environment, inexpensive and diverse metal oxide precursors, well-crystallized stoichiometric production, and varying oxidation states of the metals with applied pressure. If the applied synthesis pressure is high enough, the metal nitride could form; if the applied pressure is insufficient, then the unwanted elemental metal would be quenchable instead of the target metal nitride. Even if the metal borate byproduct is able to form, target metal nitride still fails to come into being at relatively low pressure. A good case in point is the HPSSM synthesis of rhenium nitrides [19]. The HPSSM reaction between sodium perrhenate ($NaReO_4$) and BN at 14 GPa and 1600 °C produces Re_3N as depicted in Eq. (6), whereas at 5 GPa and 1800 °C, it produces metal Re as given in Eq. (7).

Table 1
Recent advance in HPSSM Reaction.

Precursors	Reaction products	p and T conditions	Ref.
$LiGaO_2$ + BN	GaN + $LiBO_2$	1.0−5.0 GPa, 900−1400 °C	[11]
$NaGaO_2$ + BN	GaN + $NaBO_2$	1.0−5.0 GPa, 1000−1600 °C	[20]
$KGaO_2$ + BN	GaN + KBO_2	5.0 GPa, 1300−1450 °C	[19]
$NaVO_3$ + BN	VN + $NaBO_2$	5.0 GPa, 1400 °C	[19]
$NaVO_2$ + BN	VN + $NaBO_2$	5.0 GPa, 1400 °C	[19]
$NaCrO_2$ + BN	CrN + $NaBO_2$	0−5.0 GPa, 800−1400 °C	[15]
$NaFeO_2$ + BN	Fe_3N + $NaBO_2$ + N_2	5.0 GPa, 1400 °C	[19]
$Ca_2Fe_2O_5$ + BN	Fe_3N + $Ca_2B_2O_5$ + N_2	5.0 GPa, 1400 °C	[19]
$MgFe_2O_4$ + BN	Fe_3N + MgB_2O_4 + N_2	5.0 GPa, 1400 °C	[19]
Na_2CO_3 + BN	graphite + $NaBO_2$ + N_2	5.0 GPa, 1600 °C	[19]
Li_2CO_3 + BN	graphite + $LiBO_2$ + N_2	5.0 GPa, 1600 °C	[19]
$NaInO_2$ + BN	In + $NaBO_2$ + N_2	5.0 GPa, 1400 °C	[19]
$LiInO_2$ + BN	In + $LiBO_2$ + N_2	3.5 GPa, 1000 °C	[19]
$NaCoO_2$ + BN	Co_4N_x + $NaBO_2$ + N_2	5.0 GPa, 1300−1400 °C	This work
$LiNiO_2$ + BN	Ni + $LiBO_2$ + N_2	5.0 GPa, 1400−1500 °C	[19]
Na_2WO_4 + BN	W_xN + $NaBO_2$ + N_2	5.0 GPa, 600−2300 °C	[16]
Na_2MoO_4 + BN	Mo_xN + $NaBO_2$ + N_2	5.0 GPa, 400−2200 °C	[17]
K_2OsO_4 + BN	Os + KBO_2 + N_2	5.0 GPa, 1200 °C	[17]
$NaReO_4$ + BN	Re + $NaBO_2$ + N_2	5.0 GPa, 1800 °C	[19]
$NaReO_4$ + BN	Re_3N + Re + $NaBO_2$ + N_2	14.0 GPa, 1600 °C	[12,19]
Fe_2O_3 + BN	Fe_3N + B_2O_3 + N_2	5.0 GPa, 1400 °C	[18]
Fe_2O_3 + CoO + BN	$Fe_{3-x}Co_xN$ + B_2O_3 + N_2	5.0 GPa, 1400 °C	[18]
Fe_2O_3 + NiO + BN	$Fe_{3-x}Ni_xN$ + B_2O_3 + N_2	5.0 GPa, 1400 °C	[18]
$CeCl_3$ + MgO	CeOCl + $MgCl_2$	5.0 GPa, 1300−1600 °C	Unpublished results

$$3NaReO_4 + 3BN \rightarrow Re_3N + 3NaBO_2 + 3O_2 + N_2. \quad (6)$$

$$3NaReO_4 + 3BN \rightarrow 3Re + 3NaBO_2 + 3O_2 + 3/2N_2. \quad (7)$$

In most cases, the synthesis temperature (1000−1400 °C) is typically lower than the high-pressure melting points of metal-oxide precursors (1300−1700 °C) and BN (>3000 °C), but is always higher than the melting point (800−900 °C) of metal borate by-products. An HPSSM reaction for the synthesis of metal nitrides initially occurs at the intimate interface between the two solid-state precursors, and then the reaction products and by-products would be distributed in the entire high-pressure sample chamber in the form of tiny particles. Because of the relatively low melting points, the metal borates
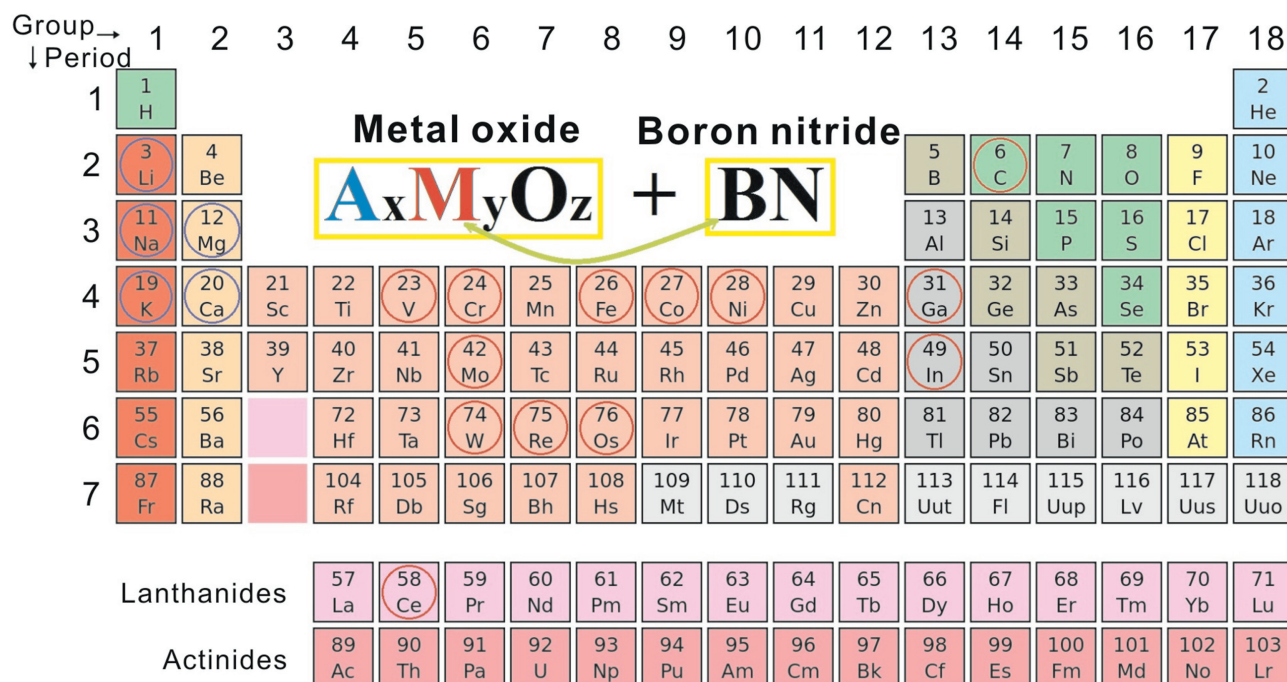

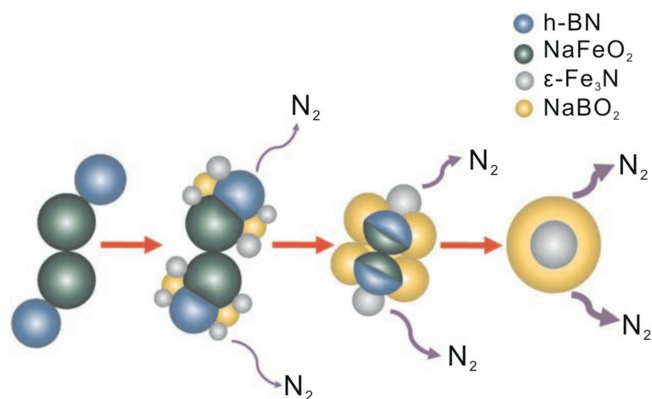Fig. 1. Elements (circled) involved in HPSSM reactions.

Fig. 2. Formation of spherical bulk ε-Fe₃N during an HPSSM reaction process [12].

would be in the molten state, serving as a kind of solvent that could speed up the diffusion and enhance the process of metal nitride product formation. The Fe_3N products in the $NaBO_2$ melt incline to gather in a spherical body. Fig. 2 shows the speculated reaction process to spherical bulk Fe_3N [12]. Small droplets combine to a single large droplet due to the effect of the lower surface energy. The HPSSM reaction between $NaFeO_2$ and BN produces spherical bulk $ε$-Fe_3N as given in Eq. (8).

$$3NaFeO_2 + 3BN \rightarrow Fe_3N + 3NaBO_2 + N_2. \qquad (8)$$
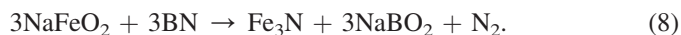
The HPSSM reaction is an effective synthetic route to boron-free metal nitrides, although BN is used for one of the reaction precursors. In HPSSM reactions, B atom tends to bond with O atom to form a boron oxide, which may have lower energy enthalpy in comparison to diffusing into metal interstitial voids forming a boron interstitial metal alloy. B cannot be detected by neutron powder diffraction (NPD) or energy-dispersive X-ray analysis (EDX), at least within the sensitivity of the instruments. The determination of nitrogen content of the metal nitride products is a challenge. In improved EDX quantitative analyses, osmium surface coating (5 nm thick) was performed with an osmium coater on the surface of the well-polished metal nitride samples as well as the EDX standard samples (corresponding metal elements and nitrogen). The EDX method used in this work can effectively improve the accuracy of the quantification of heavy and light elements (such as Fe, Co, Ni, Re, Ga and N), and the accuracy of the quantification was evaluated to be less than 0.5% [21–23]. The metal nitride products of HPSSM synthetic route are near-stoichiometric and have better crystallinity as compared with SSM reaction and high-pressure synthesis reaction.

2.3. Thermodynamic considerations

Similar to temperature and chemical composition, pressure is one of the essential factors that can influence a chemical reaction process. It is generally considered that the advantage of the use of high pressure in a chemical reaction

fundamentally lies in increasing the surface intimate contact between two reagents, enhancing the collision cross section for reaction, and preventing thermal decomposition and volatility of the reagents and products at high temperature. Actually, the effect of pressure on chemical reaction is far more than our initial recognition. Fig. 3 presents the effect of pressure on an HPSSM reaction between metal oxide (AMO) with BN. HPSSM reactions between metal oxides and boron nitride demonstrate that the nitridation of a metal-oxide precursor is a thermodynamically favored process at high pressure. The high-pressure confining environment allows nitrogen to participate in chemical reaction unhindered by the competition from oxygen. Thermodynamic investigations with the aid of density functional theory (DFT) calculations on several typical HPSSM reactions indicate that the pressure could reduce the ΔH and open a new reaction path to metal nitride products [19].

3. Recent advances in metal nitride syntheses via HPSSM reactions

3.1. 3d transition metal nitride, ε-Fe₃N, ε-Fe₃₋ₓMₓN, CrN, and Co₄Nₓ

The Earth's inner core is composed primarily of Fe element. Fe transforms from a bcc $α$-Fe at ambient conditions to an hcp $ε$-Fe over a wide range pressure (13–300 GPa) and temperature conditions (<3000 °C) [24]. $ε$-Fe_3N is a rare-nitrogen iron mineral in nature, under the name of "*Siderazot*". Recent studies have shown that spherical bulk $ε$-Fe_3N could be synthesized by HPSSM reactions at 5 GPa and 1400 °C between ternary alkaline or alkaline-earth metal ferrite ($NaFeO_2$, $MgFe_2O_4$, and $Ca_2Fe_2O_5$) and BN [19], or between binary hematite Fe_2O_3 and BN [18]. Reactions forming ternary mixed-metal nitride (e.g. $ε$-$Fe_{3-x}Co_xN$) have been achieved [18]. Fig. 4 shows the experimental assembly for HPSSM reaction between Fe_2O_3, CoO and BN producing ternary iron-

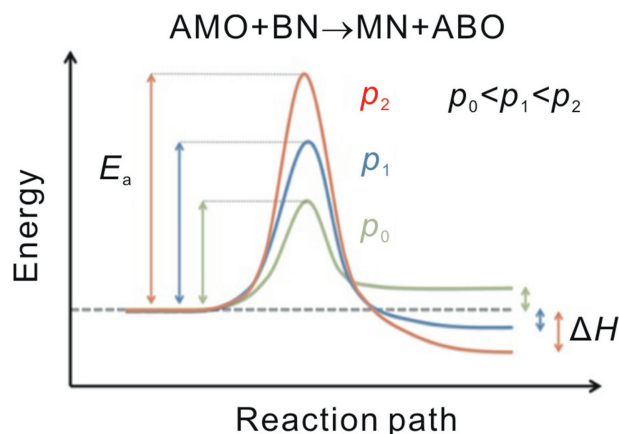
Fig. 3. Schematic potential-energy diagram showing the effect of pressure in the HPSSM reaction between AMO and BN [19]. Pressure, p, opens different reaction pathways with lower reaction enthalpy, ΔH, and higher activation energy, E_a. The dotted-line represents the energy of reaction precursors, AMO and BN.
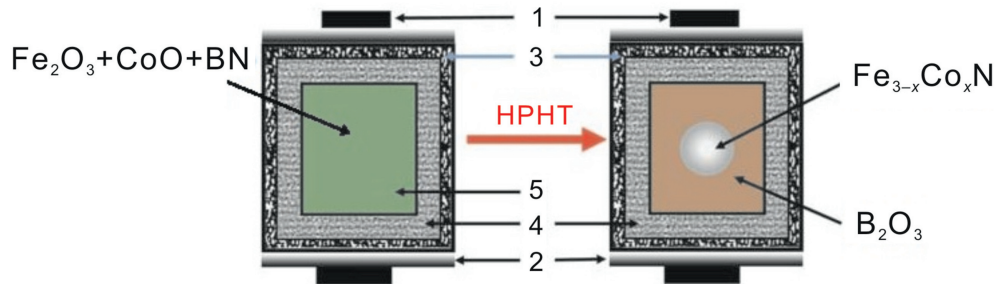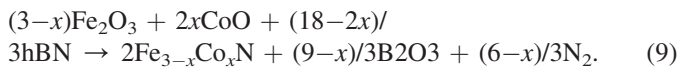
Fig. 4. Experimental assembly for HPSSM reaction for $Fe_{3-x}Co_xN$ crystals: 1—steel ring; 2—Mo sheet; 3—graphite furnace; 4—h-BN or Ta; 5—reaction precursors.

based nitrides ε-$Fe_{3-x}Co_xN$. And the reaction can be given as follows

$$(3-x)Fe_2O_3 + 2xCoO + (18-2x)/3hBN \rightarrow 2Fe_{3-x}Co_xN + (9-x)/3B_2O_3 + (6-x)/3N_2. \quad (9)$$

As depicted in Fig. 5(a), there is a 3–5 mm diameter metallic spherical bulk iron-based nitride in the recovered high-pressure cell. The formed ball-like product takes up much of the sample chamber (~8 mm in diameter). Fig. 5(b) shows the typical XRD patterns of a series of iron-based nitrides.

Chromium mononitride (CrN) exhibits interesting magnetic, structural, and electronic properties that are of fundamental importance to technological applications. To date, the preparation of bulk and stoichiometric CrN has been challenging; most products are often nonstoichiometric and poorly crystallized. Recently, CrN has been successfully prepared through HPSSM reaction between $NaCrO_2$ and BN, and the reaction is

$$NaCrO_2 + BN \rightarrow CrN + NaBO_2. \quad (10)$$

As shown in Fig. 6(a), the final CrN product is phase-pure, stoichiometric, and well-crystallized in the bulk form [25,26]. Besides, experimental results of phase stability and compressibility of CrN have also been reported. The obtained bulk moduli for cubic and orthorhombic CrN are 257 and 262 GPa, respectively [26]. However, as depicted in Fig. 6(b),

no evidence manifests the phase-transition-induced elastic softening in CrN. This result invalidates the conclusion of phase-transition-induced elastic softening reported based on nonmagnetic simulations for cubic CrN [27].

Besides, our recent studies indicate that the Co_4N_x, a 3d transition metal nitride, also can be prepared through the HPSSM reaction between $NaCoO_2$ and BN, which is

$$NaCoO_2 + BN \rightarrow Co_4N_x + NaBO_2 + N_2. \quad (11)$$

XRD pattern of the prepared Co_4N_x is shown in Fig. 7. The inset of Fig. 7 is a scanning electronic microscopy (SEM) image of the Co_4N_x product. As shown in this Figure, all the diffraction peaks can be indexed by cubic Co_4N in space group Fm3m (PDF Card 00-041-0943). By a quantitative analysis of the EDX spectrum, the approximate atomic ratio of Fe to N is 4:0.45.

3.2. 4d transition metal nitride, MoN_x

Nitrogen-rich transition-metal nitrides are a class of compounds with a wide range of properties and applications. A recent study has shown that nitrogen-rich molybdenum nitride 3R-MoN_2 with a rhombohedral MoS_2-type structure (see Fig. 8(a)) can be successfully prepared through an HPSSM reaction between $NaMoO_4$ and BN, which is

$$Na_2MoO_4 + 2BN \rightarrow MoN_2 + 2NaBO_2. \quad (12)$$
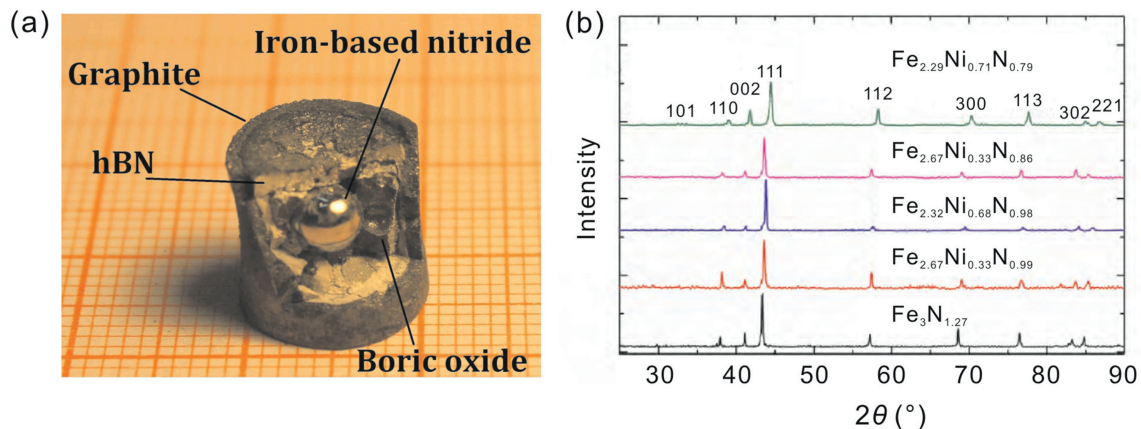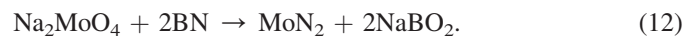

Fig. 5. (a) A high-pressure cell recovered from high-pressure experiment; (b) XRD patterns for iron-based nitrides.
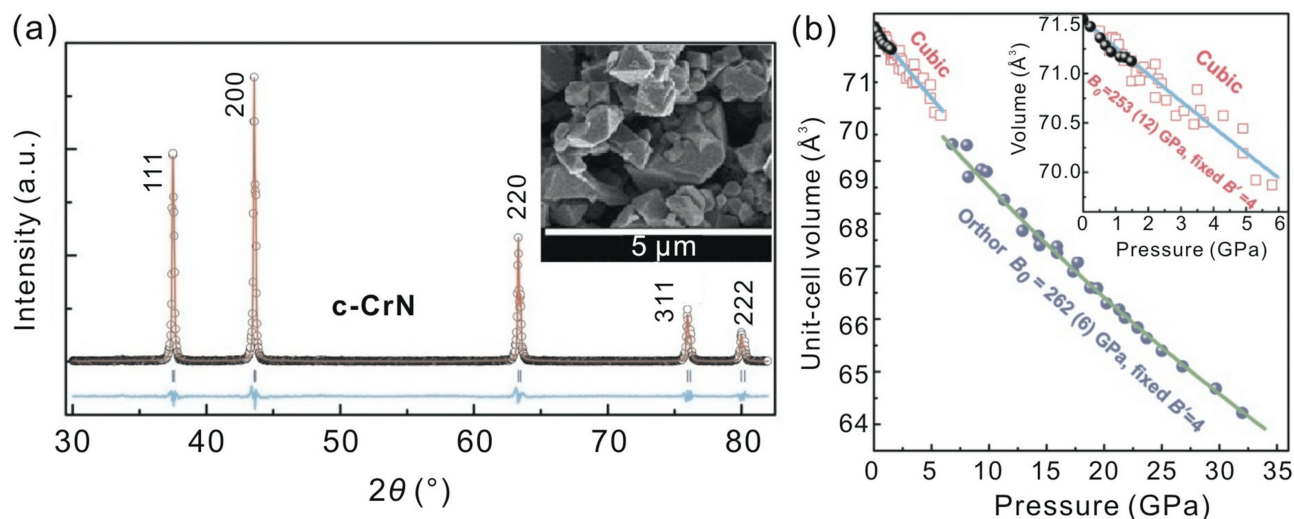
Fig. 6. (a) Refined XRD patterns for CrN, the inset is a typical SEM image for CrN crystals; (b) Volume–pressure data of cubic- (open pink squares) and orthorhombic-CrN (solid blue circles). The inset is an enlarged portion of data for c-CrN. Solid black circles represent the data obtained from high-p neutron-diffraction experiments (0–2 GPa).

Fig. 8(b) shows the catalytic activities of the prepared 3R-MoN_2 in H_2 atmosphere. Experimental results show that this new nitride exhibits catalytic activities that are three times more active than the traditional catalyst MoS_2 for the hydrodesulfurization of dibenzothiophene and more than twice as high as in the selectivity to hydrogenation [17]. The conclusion that the nitride is catalytically active in sour methanation of syngas with >80% CO and H_2 conversion at 723 K was also obtained in Ref. [17].

Also, a recent study shows that hexagonal δ-MoN and cubic γ-MoN can be prepared through an HPSSM reaction between $NaMoO_4$ and BN, where the reaction is given as

$$Na_2MoO_4 + 2BN \rightarrow MoN + 2NaBO_2 + 1/2N_2. \quad (13)$$
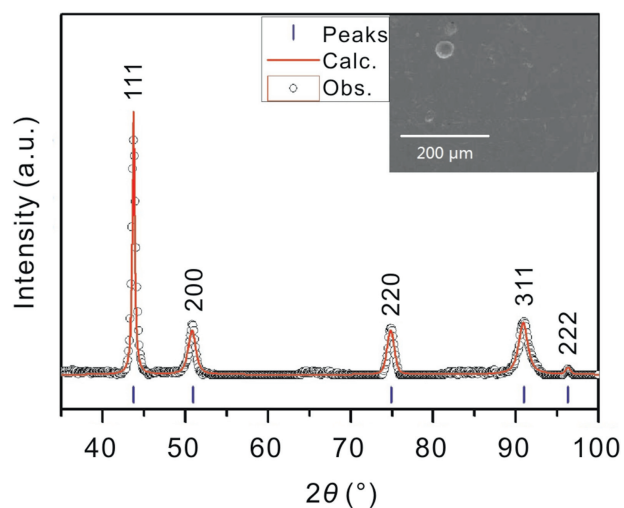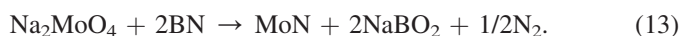

Fig. 7. XRD patterns of Co_4N_x samples. Open black circles and solid red lines represent the observed and calculated profiles, respectively. The inset shows the SEM photograph of Co_4N_x sample.

Fig. 9(a) shows the XRD patterns of hexagonal δ-MoN and cubic γ-MoN. Based on single crystal measurements, as shown in Fig. 9(b), the hexagonal δ-MoN and cubic γ-MoN exhibit excellent hardness of ~30 GPa and ~23 GPa, respectively. Consistent with previous studies, the measured superconducting transition temperatures for δ-MoN and cubic γ-MoN are 13.8 K and 5.5 K, respectively. It indicates that δ-MoN is so far the hardest metal nitride with the second highest T_c, comparable to that of NbN (~16 K).

3.3. 5d transition metal nitride, Re_3N and WN_x

Since the discovery of PtN_2 in 2004, there has been a rapidly growing interest in synthesis and characterization of novel 5d transition metal nitrides. The synthesis of well-crystallized Re_3N is still a great challenge due to the demanding synthetic conditions and the lack of effective synthetic route. Well-crystallized plate-like Re_3N crystals were synthesized through an HPSSM reaction between $NaReO_4$ and BN in large volume press (LVP) at 14 GPa and 1973 K. The chemical reaction equation can be depicted as

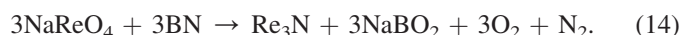$$3NaReO_4 + 3BN \rightarrow Re_3N + 3NaBO_2 + 3O_2 + N_2. \quad (14)$$

Fig. 10(a) shows the XRD pattern and an SEM image of the Re_3N products. Except for some small diffraction peaks of hexagonal Re, all the other diffraction peaks can be indexed by hexagonal Re_3N in space group P-6m2. Consistent with the values reported by Friedrich et al. [6], the refined cell parameters of Re_3N are $a = 2.811(1)$ Å and $c = 7.139(5)$ Å. As shown in the inset of Fig. 10(a), Re_3N crystallizes in hexagonal plate-like shape of a diameter of ~200 nm and a thickness of ~20 nm. It was also found that the Grüneisen parameters for Raman modes of Re_3N, as shown in Fig. 10(b), were substantially larger than the previously calculated values [6].
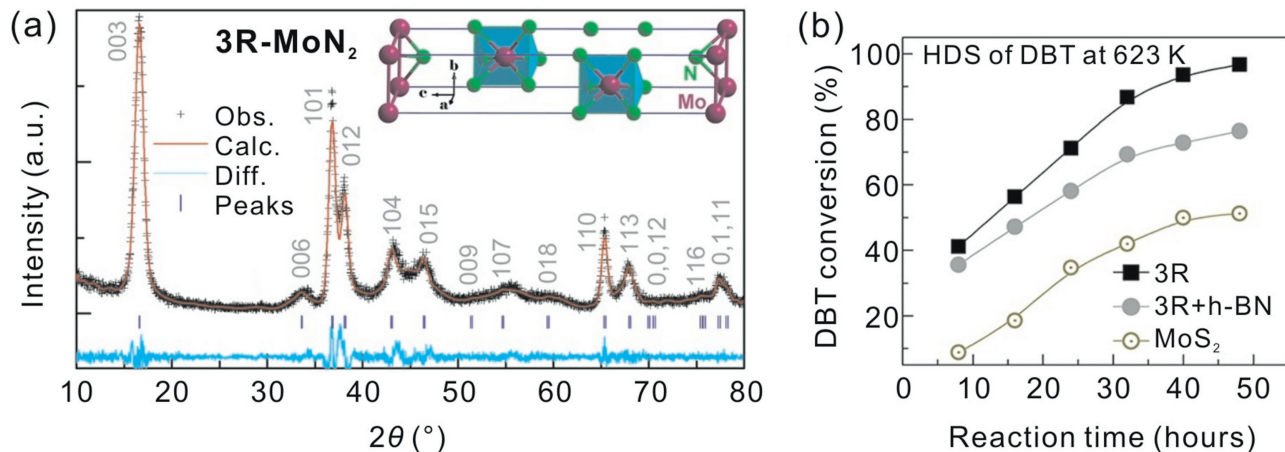
Fig. 8. (a) Refined XRD pattern for 3R-MoN$_2$. Inset is a polyhedral view of the 3R-MoN$_2$ structure. (b) Catalytic activities of 3R-MoN$_2$ in the hydrodesulfurization (HDS) of dibenzothiophene (DBT) in H$_2$ atmosphere.
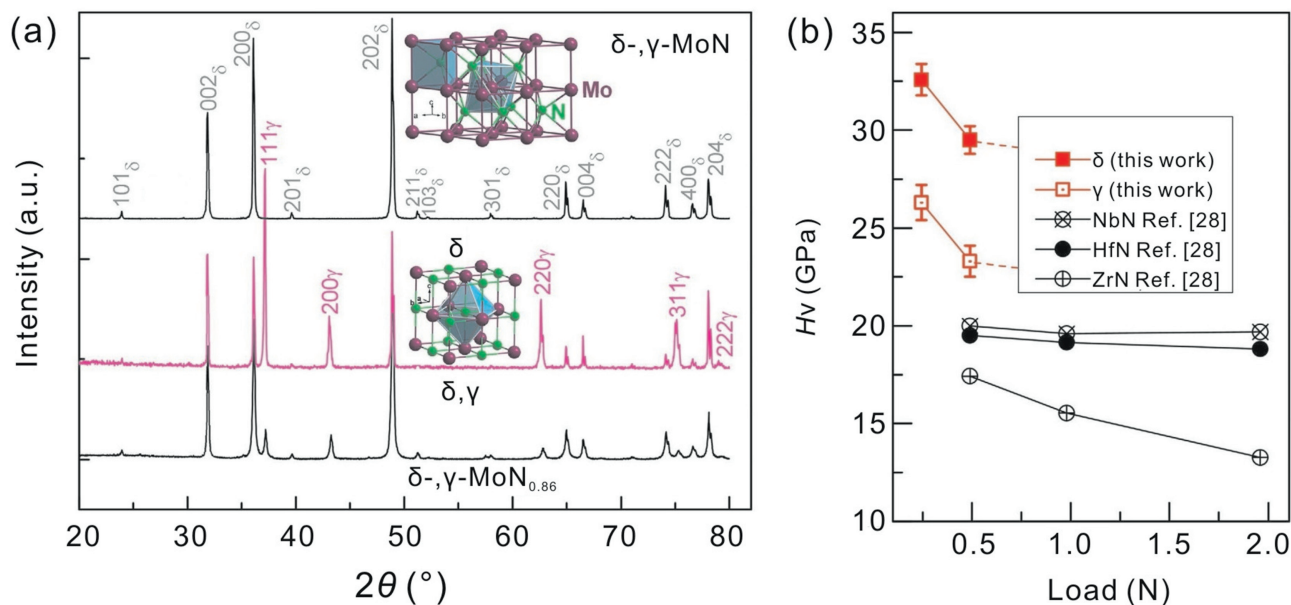

Fig. 9. (a) XRD patterns for δ- and γ-MoN. (b) Vickers hardness of δ- and γ-MoN as a function of applied load compared with ZrN, NbN, and HfN (Ref. [28]).
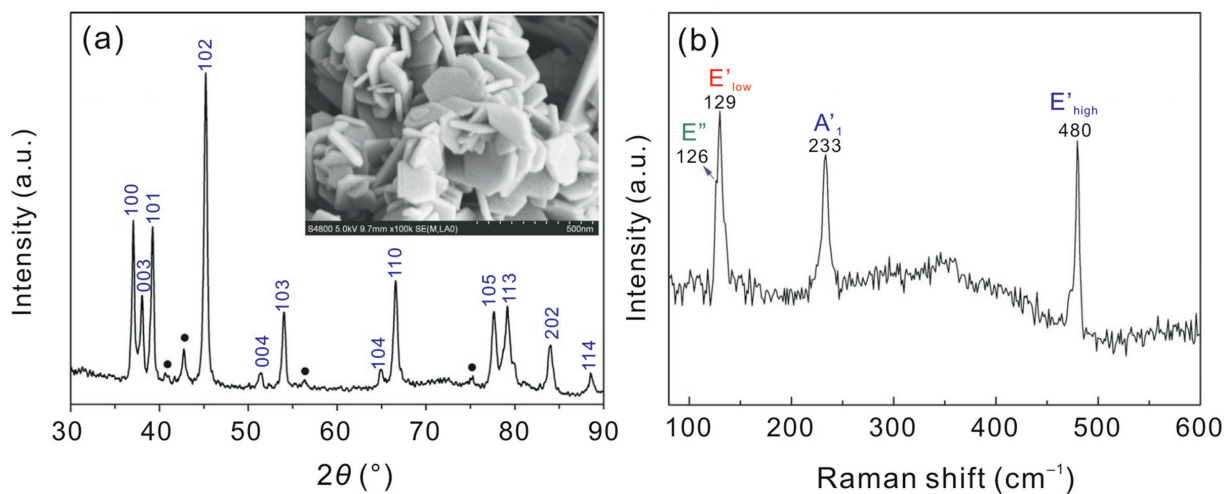

Fig. 10. (a) Powder XRD pattern of purified Re$_3$N samples. The circles indicate the diffraction peaks of Re. The inset shows a typical SEM photograph of Re$_3$N sample; (b) The ambient Raman spectrum of synthesized Re$_3$N crystals.
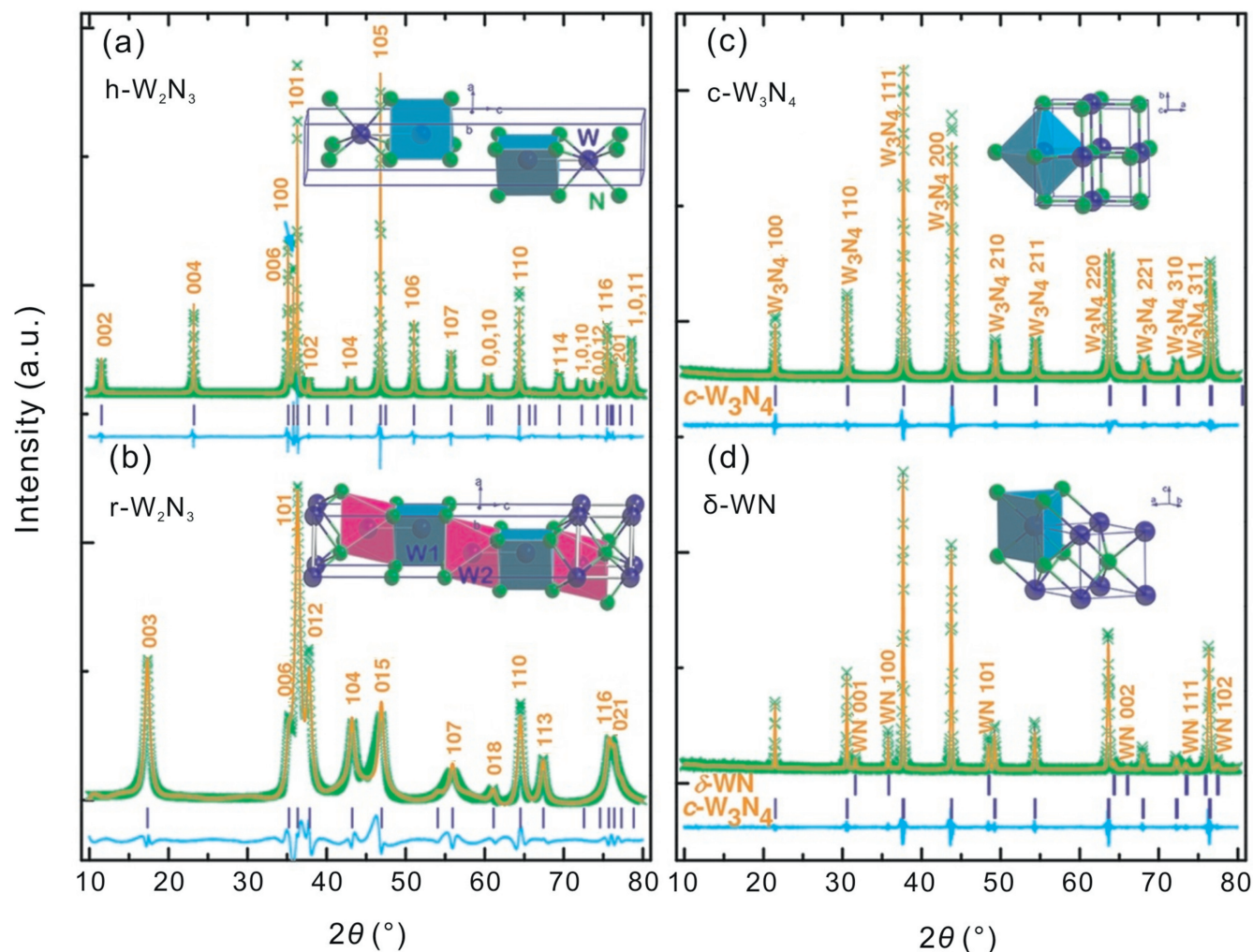
Fig. 11. XRD patterns of nitrides in the binary system W-N. The observed (green crosses) and calculated (solid orange lines) profiles for (a) h-W_2N_3, (b) r-W_2N_3, (c) c-W_3N_4 and (d) δ-WN respectively.

Tungsten nitrides have recently attracted considerable interest because of their unique and/or superior chemical, mechanical, and thermal properties. To date, however, most materials in the W-N system are in the form of thin films and are often poorly crystallized, which severely limits their use in diverse technological applications. A recent study indicates that WN_x can be prepared through an HPSSM reaction [16]. Fig. 11 shows the XRD patterns of the prepared binary h-W_2N_3, r-W_2N_3, c-W_3N_4 and δ-WN respectively. The chemical reaction equation can be depicted in Eqs. (15–17).

$$2Na_2WO_4 + 4BN \rightarrow W_2N_3 + 4NaBO_2 + 1/2N_2. \qquad (15)$$

$$3W_2N_3 \rightarrow 2W_3N_4 + 1/2N_2. \qquad (16)$$

$$W_3N_4 \rightarrow 3WN + 1/2N_2. \qquad (17)$$

The final products are phase-pure and well-crystallized in bulk forms. It is found that hexagonal W_2N_3, hexagonal WN, and cubic W_3N_4 exhibit elastic properties rivaling or even exceeding cubic-BN and other novel transition metal nitrides.

In addition to transition metal nitrides, other metal compounds can also be prepared through HPSSM reactions. Here is an example, as our recent research shows that CeOCl, a potential semiconductor material, can be prepared by a novel HPSSM reaction between MgO and $CeCl_3$ powders at 5 GPa and 1873 K. The chemical reaction equation can be depicted as follows,

$$CeCl_3 + MgO = CeOCl + MgCl_2. \qquad (18)$$

4. Conclusion

A recent advance in HPSSM reactions is presented for the syntheses of transition metal nitrides. Our results strongly suggest that the high-pressure confining environment thermodynamically favors the formation of well-crystallized transition metal nitrides products through HPSSM reactions, which is theoretically supported by density functional theory (DFT) calculations. A chemical reaction that cannot occur at atmospheric pressure can take place at high pressure, opening a new effective pathway to material synthesis and design. Hopefully, more novel compounds with

excellent properties can be prepared through HPSSM reactions in the future.

Conflict of interest

The authors declare that there is no conflicts of interest.

Acknowledgements

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