Facile and General Route to Nitrides by a Modified Solid-State Metathesis Pathway

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Received November 23, 2006. Revised Manuscript Received January 5, 2007

We have developed a modified solid-state metathesis method by selecting metal oxides and Li_3N as precursors to prepare nitrides in sealed ampoules or tube furnace, which provide a general, facile, and high-efficient route to most binary metal nitrides including III-nitrides, transition metal nitrides, rare-earth nitrides, and some ternary metal nitrides. A two-step process is involved in this route and thermodynamical favored byproduct Li_2O serves as a potent driving force, enhancing the nitrides formation process. Our results show that this route offers an attractive preparative route to nitrides due to the wide availability of metal oxides, high yield, and relatively simple operation.

I. Introduction

Metal nitrides have been attracting much attention due to their useful properties such as wide band-gap, abrasive resistance, hardness, or electrical conductivity.[1] For example, GaN is one of the most important wide-band semiconductors in the fabrication of short-wavelength optoelectronic devices such as the blue/green light emitting diodes (LEDs), violet laser diodes (LDs), and flat-panel display.[2] AlN shows its prominent application in the field of ultraviolet (UV) photodetectors, field-effect transistors (FET), thermal radiation sensors, and pressure sensors.[3] Recently, some rare-earth nitrides, for instance, GdN as a potential candidate for spin electronics material, have become an active research area in past years in the field of fundamental research.[4] Some new transition metal nitrides, IrN_2 and OsN_2, have been predicated to be potential superhard materials with bulk modulus $K_0 = 428$ GPa, recently.[5] Other applications of nitrides include high-temperature ceramics, catalysts, or tool coatings.

In general, metal nitrides are synthesized by the reactions of metal or metal oxides with ammonia directly.[6] This process usually requires high temperatures and long reaction durations. Incomplete conversions or decompositions of the products are often encountered in this process. In the past decade, solid-state metathesis (exchange) reaction (SSM) has been developed to efficiently prepare a variety of materials including nitrides, sulfides, and carbides.[7] More recently, Zhao et al.[8] reported a route to prepare nitrides employing g-C_3N_4 as nitridation reagent and a carbothermal reduction process was involved. However, residual carbon, low yields, and limited nitridation power to more nitrides are the problems that still need to be tackled with. Other existing methods for preparation of nitrides, such as gas-phase/solid-state precursors decomposition and organic solvothermal process, are also confined by the preparation of certain nitrides by various drawbacks such as poor crystallinity or presence of impurity.[9] Therefore, it is still desired to develop a more general route to most nitrides, which meets the increasing demand of nitrides in a variety of applications.

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10.1021/cm062796s CCC: $37.00

Table 1. Formation Conditions and Structural Information for Binary Nitrides Synthesis in this Study

processors (amounts)	ratio oxide/Li_3N	chemical yield	reaction temp (K)	reaction time (h)	products[a] (PDF card no.)	cell constant (Å)
Al_2O_3 (11.4 mmol)	1:2.2	0.75	1023	4	AlN (25-1133)	$a = 3.1095(2)$, $c = 4.9722(3)$
Ga_2O_3 (8.51 mmol)	1:2.2	0.91	973	3	GaN (50-0792)	$a = 3.1865(2)$, $c = 5.1803(3)$
Cr_2O_3 (17.1 mmol)	1:2.2	0.92	973	2	CrN (65-2899)	$a = 4.1406(2)$
ZrO_2 (7.51 mmol)	1:1.2	0.90	1123	3	ZrN (65-2905)	$a = 4.5198(2)$
TiO_2 (7.51 mmol)	1:1.5	0.89	1023	3	TiN (038-1420)	$a = 4.2228(6)$
V_2O_5 (2.64 mmol)	1:4.3	0.88	1123	3	VN (65-0437)	$a = 4.1233(9)$
Nb_2O_5 (2.26 mmol)	1:4.3	0.83	1123	3	NbN (74-1218)	$a = 4.3276(7)$
Ta_2O_5 (3.32 mmol)	1:4.3	0.85	1123	3	TaN (49-1283)	$a = 4.3286(2)$
B_2O_3 (5.70 mmol)	1:2.2	0.82	1123	4	BN (45-0896)	
La_2O_3 (5.19 mmol)	1:2.2	0.92	1123	3	LaN (65-7475)	$a = 5.2762(6)$
CeO_2 (5.71 mmol)	1:1.2	0.91	1123	3	CeN (65-2914)	$a = 4.9952(9)$
Eu_2O_3 (5.19 mmol)	1:2.2	0.92	1123	3	EuN (65-1701)	$a = 4.9642(7)$
Gd_2O_3 (3.60 mmol)	1:2.2	0.93	1123	3	GdN (65-1700)	$a = 4.8102(4)$
Yb_2O_3 (5.50 mmol)	1:2.2	0.89	1123	4	YbN (65-0494)	$a = 4.7616(8)$
Sm_2O_3 (5.19 mmol)	1:2.2	0.89	1123	4	SmN (65-1702)	$a = 4.9577(2)$
Er_2O_3 (5.19 mmol)	1:2.2	0.88	1123	4	ErN (65-5799)	$a = 4.8213(4)$
Ho2O3 (5.19 mmol)	1:2.2	0.87	1123	3	HoN (65-5980)	$a = 4.8694(8)$

[a] All samples crystallize in $Fm\bar{3}m$, except AlN ($P6_3mc$), GaN ($P6_3mc$), NbN ($F23$), and BN ($P\bar{3}m1$).

Compared with halides used in SSM routes, oxides are more chemically stable, cheaper, and more common in nature. However, the preparation of nitrides using oxides and alkali metals or alkaline-earth metal nitrides as precursors has been less investigated. Up to now, few examples are known in this aspect. The first nitride formed by a reaction of oxides and Li_3N as precursors is CrN, reported by Parkin and others,[10] and then, GaN is obtained through a reaction of Ga_2O_3 and Li_3N in a nitrogen atmosphere by Kamler et al. and Mabuchi et al.[11] The limited number of investigations on the reactions using oxides as precursors and Li_3N as nitridation reagent suggest that we explore this pathway as a general route to nitrides. Here, we show this process to be an extremely powerful route to most binary metal nitrides and some ternary nitrides. A possible mechanism is proposed to explain the experimental results. This route is considered to be a modified solid-state metathesis (MSSM) process; some new characteristics are involved in this route.

II. Experimental Section

Synthesis and Purification. All oxides involved were of spectral grade. Li_3N was synthesized by the reaction of metallic Li (99.9%) and N_2 (99.999%) in a quartz tube at about 400 °C. In a typical run, α-Al_2O_3 (99.999%) was used as the precursor to react with Li_3N with the molar ratio of 1:2.2 (α-Al_2O_3:Li_3N) Here, 10% Li_3N in excess was used to ensure the complete conversion of alumina. The excess Li_3N and byproduct Li_2O could be thoroughly removed by deionized water. Typically, 1.1661 g of the α-Al_2O_3 (99.999%) and 0.8802 g of the Li_3N were mixed in an agate mortar and ground together. Then the starting materials were pressed to a pellet and put into a stainless steel crucible (inner diameter 13 mm, outer diameter 14 mm, length 30 mm), followed by placing the crucible into a silica ampule connected to an evacuating system. When evacuated to 3×10^{-5} Pa, the silica ampule was filled with high-purity nitrogen (99.999%) up to 0.3 atmospheric pressure and sealed. In succession, the silica ampule was heated to 1073 K in the muffle at the rate of 200 K/h and maintained for 2 h. Then the power was shut off and the muffle was cooled down to room temperature (RT) naturally. The yellowish powder obtained was rinsed with deionized water (20 mL) and ethanol solution (40 mL), and then large scale products were isolated using filtration and were dried in air. Similarly, 0.6000 g of the TiO_2 (99.999%) and 0.4000 g of the Li_3N with a molar ratio of 1:1.5 (TiO_2:Li_3N) were heated to 1073 K for 3 h to prepare TiN. Then 1.9636 g of Ho_2O_3 (99.9%) and 0.4000 g of the Li_3N were ground together and maintained at 1123 K for 2 h to obtain HoN. Here, rare-earth nitrides could hydrolyze slowly, and the products should be treated by ethanol solution and vacuum filtration only.

Product Characterization. The phase identifications of the products were carried out in a MAC-M18XHF diffractometer with Cu Kα radiation (50 kV × 200 mA, $\lambda = 1.5418$ Å) and a graphitic monochromator. The morphology of the products were examined by a field emission scanning electron microscopy (FE-SEM, FEI XL 30 S-FEG) and composition analysis was conducted using an energy-dispersive spectroscope (EDX) attached to the FE-SEM. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (Philips CM 200FEG) were used to further investigate the morphology, size, and structure of the samples at 120 and 200 kV, respectively. Samples were suspended in ethanol under ultrasonic vibration and a drop of the suspension was brought onto a holey super-thin carbon film on a copper grid.

III. Results and Discussion

Table 1 lists the formation conditions and structural information for the obtained binary nitrides in this study including III-nitrides (GaN, AlN, BN), transition metal nitrides (TiN, ZrN, VN, NbN, TaN, CrN), and rare-earth nitrides (CeN, EuN, GdN, YbN, ErN, SmN). The MSSM reaction mechanism, using oxides and Li_3N as precursors, can be depicted by a general equation as follows:

$$M_xO_y + \frac{2y}{3}Li_3N \rightarrow yLi_2O + xMN + \frac{2y-3x}{6}N_2 \qquad (1)$$

From eq 1, we know that no nitrogen will release if $2y - 3x = 0$. This is the case with the three-valence metal oxide.

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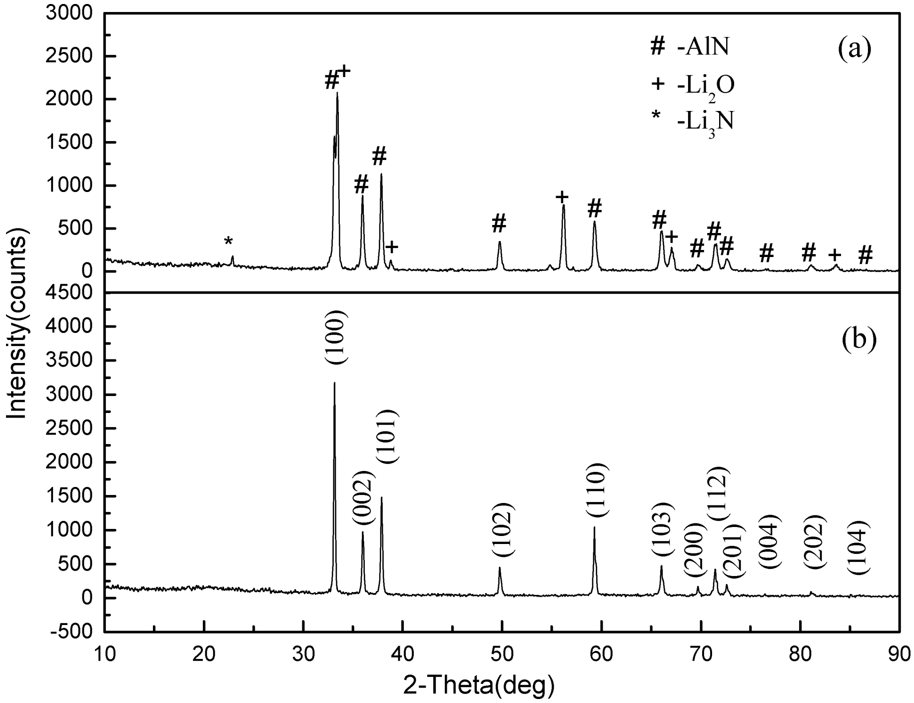

Figure 1. PXRD patterns of AlN (a) unwashed products and (b) washed products. * indicates excess Li_3N, + indicates byproduct Li_2O, and # denotes hexagonal AlN in the product.

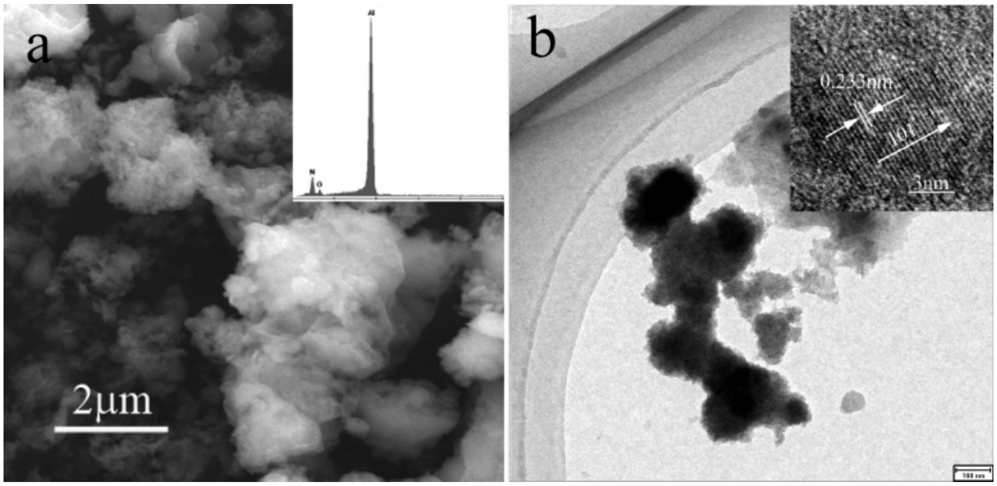

Figure 2. (a) SEM image of the AlN product after rinsing; inset is the energy dispersive X-ray analysis (EDX). (b) Low-magnification TEM images of the as-prepared AlN powder after rinsing; inset is the HRTEM lattice images of the synthesized AlN after rinsing.

Then eq 1 reduces to a typical SSM reaction. For oxides with $2y - 3x > 0$, corresponding to these with valences not equal to 3, such as M = Ti, Zr, Ce, V, Nb, or Ta. Nitrogen will be present in products, suggesting a redox process involved in the reaction. Like in SSM, exothermicity is expected in these reactions because of the formation of thermodynamical favored Li_2O in products regardless of the releasing of nitrogen or not. The thermodynamic calculation of the enthalpies of these reactions (ΔH_{rxn}) supports this point. For example, here, the calculated ΔH_{rxn} for GaN is −1016 kJ/mol by the reaction of Li_3N and Ga_2O_3, larger than that of −515 kJ from the reaction of Li_3N and GaI_3.[12]

To test the feasibility and effectiveness of this route, we first show the synthesis of AlN from α-Al_2O_3, which usually requires much higher temperatures to be prepared in other methods.[13] The powder X-ray diffraction (PXRD) patterns of products before and after rinsing are shown in Figures 1a and 1b, respectively. The PXRD pattern (Figure 1a) indicates that the products are composed of three crystalline phases, that is, hexagonal (wurtzite) AlN (ICDD-PDF: 25-1133), cubic Li_2O (ICDD-PDF: 65-2972), and hexagonal Li_3N (ICDD-PDF: 65-1896). The PXRD pattern in Figure 1b could be indexed well with hexagonal AlN and no other peaks from impurities are detected under the X-ray diffractometer's resolution, confirming eq 1. The existence of Li_3N is due to the excess precursor in the reaction. Energy dispersive X-ray analysis (EDX) (the inset in Figure 2a) shows the product consists of Al, N, and O elements and the atomic ratio of N:Al is about 39:52, revealing N deficient

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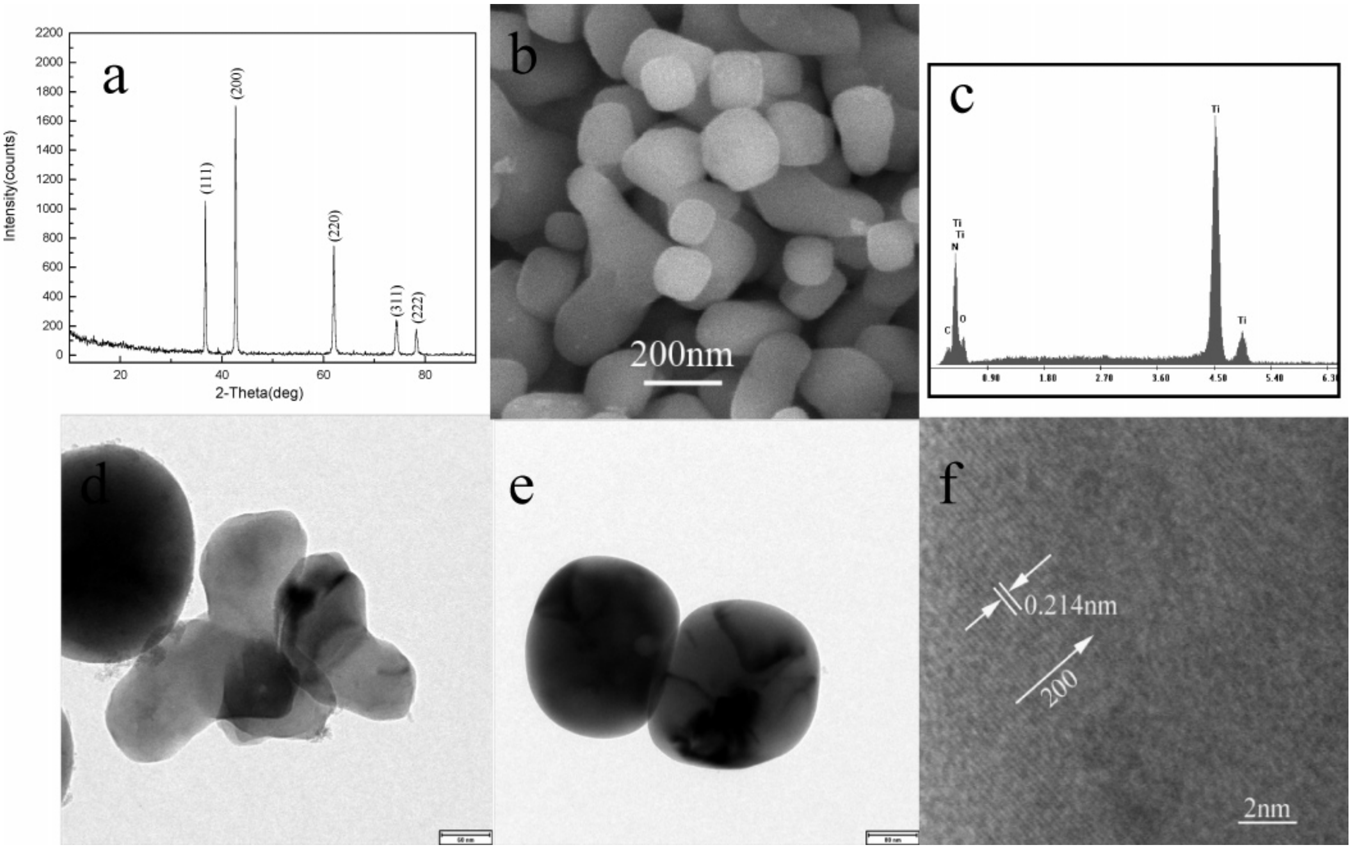

Figure 3. (a) PXRD patterns of TiN after rinsing. (b) SEM image of the TiN product after rinsing; (c) energy dispersive X-ray analysis (EDX) of the product after rinsing; (d,e) low-magnification TEM images of the as-prepared TiN powder after rinsing; (f) HRTEM lattice images of the synthesized TiN.

in the samples. The O element probably originates from the O_2 and H_2O adsorbed on the sample surfaces. It indicates that byproduct Li_2O and excess Li_3N can be effectively eliminated by a simple washing process. One highlight of this route is utilizing the solubility of the byproduct Li_2O to access high-purity nitrides and similar high-temperature metathesis mechanisms have been reported by Seshadri et al. and Gopalakrishnan et al.[14] The SEM image (Figure 2a) shows the washed AlN product is composed of fluffy, micrometer-sized powder. The typical TEM images in Figure 2b further reveal the sample is composed of some well-crystallized particles. The corresponding HRTEM image (the inset in Figure 2b) displays the lattice fringes distinctly with an interplanar spacing of 0.233 nm, which matches well with the d_{101} value of hexagonal AlN, providing further evidence for the formation of AlN. It should be noted that the α-Al_2O_3 cannot be converted into AlN by carbothermal reduction process using g-C_3N_4, revealing the potent nitrification ability of Li_3N.[8]

In another run, TiN is obtained successfully by a similar route. A redox process reducing Ti^{4+} to Ti^{3+} is revealed in this reaction. Figure 3a shows the PXRD pattern for the products after rinsing. All the diffraction peaks in the spectrum are well-indexed to be a cubic phase and the lattice parameter is calculated to be $a = 4.2228(6)$ Å, which is in good agreement with cubic TiN (ICDD-PDF: 038-1420; $a = 4.242$ Å). SEM image (Figure 3b) reveals the particles exhibiting uniform regular shape. EDX result (Figure 3c) demonstrates the products contain Ti, N, and some trace impurity O element. The low-magnification TEM images (Figures 3d and 3e) reveal the rinsed products consisting of well-crystallized particles with sizes ranging from 100 to 300 nm. From these regular morphologies, it is speculated that the formation process of TiN is close to the equilibrium state. HRTEM (Figure 3f) study unravels more detailed structural and morphological information, showing the lattice with good crystallinity, no cluster or other crystalline domains embedded, only some negligible defects in the lattice planes, and the interplanar spacing of the lattice planes being 0.214 nm, which corresponds to the (200) lattice planes of cubic TiN.

In synthesis of VN, NbN, TaN, and CrN, low valence oxides such as VO, V_2O_3, NbO, TaO, TaO_2, or CrO_2, and some mononitrides including Cr_2N or Ti_2N are often encountered in lower temperature and less Li_3N dosage, suggesting the route is a two-step process. That is, the active lithium atoms, originating from the partial decomposition of Li_3N, reduce oxides to element gradually. Then the element is nitrified by active nitrogen atoms or Li_3N directly. The heat released in the reaction also propagates more Li_3N to decompose to accelerate the reaction.

The SSM reactions are considered to be as a chain reaction, and the theoretical maximum temperature can be calculated. For instance, the maximum temperature in the preparation of GaN by the SSM route using GaI_3 and Li_3N is 1443 K, exceeding the GaN decomposition temperature of 1150 K.[12] Consequently, GaN cannot be obtained without the assistance of additives to lower the reaction temperature. In our route,

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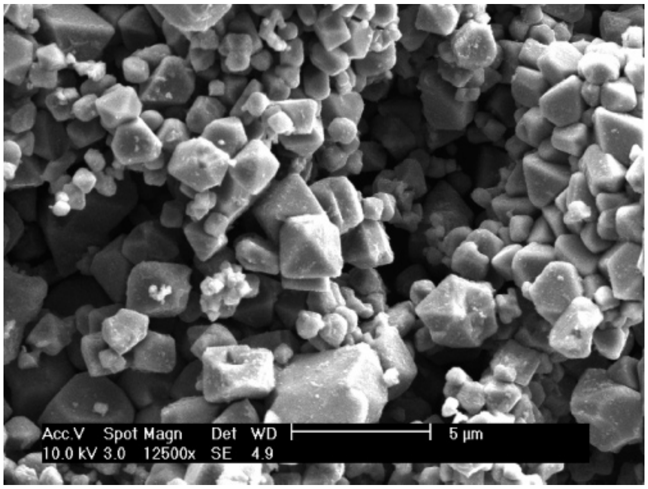

Figure 4. SEM images of the VN powder after rinsing.

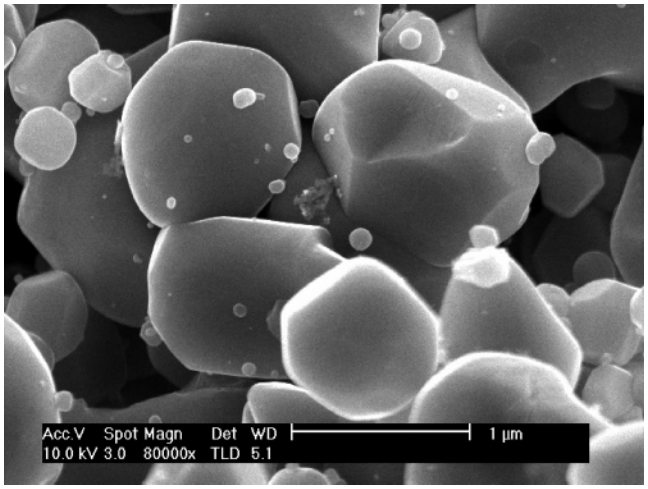

Figure 5. SEM images of the CrN powder after rinsing.

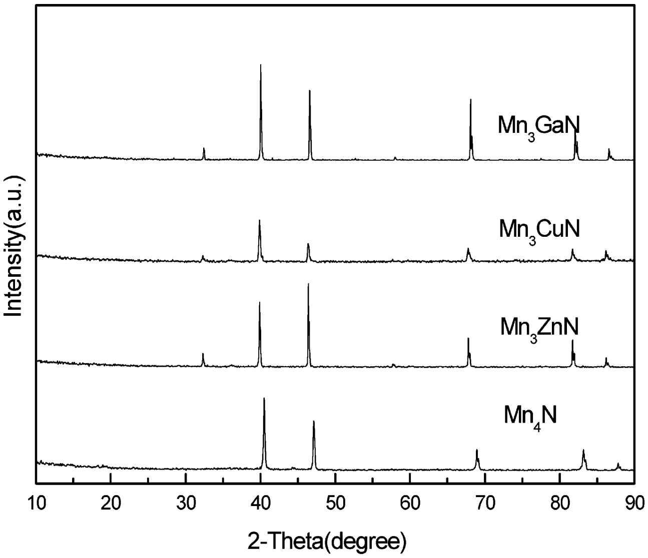

Figure 6. PXRD pattern of Mn_3XN (X = Ga, Zn, Cu) and Mn_4N.

highly crystalline GaN is obtained without the help of any additives. It is speculated that it is difficult to melt the byproduct Li_2O with a melting point of 1843 K to form solution; therefore, the diffusion process is hampered heavily by the existence of solid-state Li_2O, resulting in slower diffusion rates of the reactants and a prolonged reaction duration. The chain reaction cannot be initiated in this condition and rapid heat dissipation carries out adequately, and finally, the actual temperature does not exceed the decomposition temperature of GaN. The SEM image of the unwashed GaN shows no similar smooth continuous surface, expected for the liquid-state LiCl or LiI melt in the SSM reaction, in this route. This provides evidence to confirm our assumption of the reaction mechanism. This route offers a convenient pathway to some nitrides with low decomposition temperature that could not exist in the process of SSM routes. For these novel features, this route using oxides and Li_3N as precursors is considered to be a modified solid-state metathesis (MSSM) route. Morphologies of other produced binary nitrides such as VN and CrN are shown in Figures 4 and 5, respectively.

A striking and important feature of the MSSM route is that it can be readily extended to prepare some ternary nitrides. Take the synthesis of anti-perovskite structure Mn_3XN (X = Ga, Zn, Cu, Cr, Sn, etc.), for instance, which holds promise for applications with negative thermal expansion.[15] The general reaction to these compounds can be written

$$3x\mathrm{Mn} + \mathrm{X}_x\mathrm{O}_y + \frac{2y}{3}\mathrm{Li}_3\mathrm{N} \rightarrow x\mathrm{Mn}_3\mathrm{XN} + y\mathrm{Li}_2\mathrm{O} + \frac{2y-3x}{6}\mathrm{N}_2 \quad (2)$$

In this type of reaction, the oxides are first reduced to metals and then combine with Mn and N atoms to form Mn_3XN. Therefore, the MSSM route includes not only the metathesis but also the addition reactions, providing further information for a two-step process. The formation of byproduct Li_2O and the probable nitrogen gas drive the reaction to proceed. The PXRD patterns of the obtained Mn_3XN (X = Ga, Zn, Cu) products are shown in Figure 6. An alternation explanation for eq 2 is based on the reaction of Mn and Li_3N. It was found that Mn atoms can be nitrified directly by Li_3N to form the Mn_4N structure. Thus, it is speculated that the Mn atoms react with Li_3N to form Mn_4N structure, then the Mn atoms located at the corner position of Mn_4N were replaced by the metal atoms reduced by Li_3N from oxides to form the Mn_3XN system, as depicted in eq 3.

$$3x\mathrm{Mn} + \mathrm{X}_x\mathrm{O}_y + \frac{2y}{3}\mathrm{Li}_3\mathrm{N} \rightarrow \frac{3x}{4}\mathrm{Mn}_4\mathrm{N} + x\mathrm{X} + y\mathrm{Li}_2\mathrm{O} + \frac{8y-9x}{24}\mathrm{N}_2 \rightarrow x\mathrm{Mn}_3\mathrm{XN} + y\mathrm{Li}_2\mathrm{O} + \frac{2y-3x}{6}\mathrm{N}_2 \quad (3)$$

The yield mostly depends on the volume of the reactor and the byproduct can be eliminated easily. These features are not common in other existing methods. Preparations are also successfully performed in a tube furnace under a flowing

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nitrogen atmosphere, revealing the extensive applicability of the MSSM route convincingly.

IV. Conclusions

The MSSM route offers a convenient method for synthesizing an extensive range of nitrides including a large number of binary nitrides and some ternary nitrides. The results demonstrate that it is a facile, general, and high-yield route to approach nitrides. The fascination with this route is the vast range of potential precursors of oxides, and simple manipulation to access high-purity products. The use of a soluble byproduct of high melting point is significant in the development of new materials.

Acknowledgment. This work is supported by the National Natural Science Foundation of P. R. China (Grant Nos. 50372081 and 50502039) and the Hundred Talents Project of the Chinese Academy of Sciences.

Supporting Information Available: Powder XRD patterns, TEM images, and EDX patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

CM062796S