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Rapid In Situ Investigation of Nitride Synthesis: Ambient Atmospheric Nitridation of 3d Metal Oxides Using Dicyandiamide

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Abstract: The synthesis of metal nitrides, which are a class of functional materials, generally requires an air-free atmosphere, hindering their efficient exploration and production. In this study, we demonstrate the rapid screening of the nitridation conditions of 3d transition metal oxides under an ambient atmosphere via in situ synchrotron X-ray diffraction (XRD). Among V_2O_5 , $NaVO_3$, and a mixture of NH_4VO_3 and $NaHCO_3$ as the precursors and dicyandiamide as the nitrogen source, in situ XRD analysis shows that $NaVO_3$ is a suitable precursor to form a single-phase rock salt structure, which is an anion-rich oxynitride, $V_{0.69}N_{0.53}O_{0.47}$. The nitridation of $NaFeO_2$ with dicyandiamide results in the formation of Fe_3N through $FeNCN$, which is converted to Fe_3C after further heating. The reaction of $NaMnO_2$ affords $MnNCN$, while $NaCrO_2$ does not produce chromium nitride/carbodiimide. Guided by the in situ XRD results, these metal oxides and dicyandiamide are placed in an alumina crucible and heated in a box furnace under an ambient atmosphere to synthesize nitride/carbodiimide/carbide on a gram scale without a gas cylinder. This study presents a novel and efficient method for synthesizing various nitrides, oxynitrides, carbodiimides, and carbides under ambient conditions using in situ synchrotron XRD and box furnace, thereby significantly simplifying the nitride synthesis process.

1. INTRODUCTION

A variety of metal nitrides with various characteristics, including magnetic,¹ superconducting,² and catalytic properties, have been discovered over the past century.^{3,4} The triple bonds of nitrogen molecules are stronger and less reactive than the double bonds of oxygen molecules. Therefore, in contrast to the synthesis of oxides, it is challenging to produce nitrides by directly reacting nitrogen with metals under an ambient pressure.⁵ Because of this synthetic difficulty, it is essential to create an atmosphere with a low oxygen pressure.

Advances in nitride chemistry have largely depended on their synthesis. To date, various nitride synthesis processes have been developed, including high-temperature and high-pressure synthesis,⁶ high-temperature ammonolysis,⁷ combustion synthesis^{8,9} of powder/bulk samples, and the physical/chemical vapor deposition of thin films.^{10,11} The Na flux method, which was developed by Francis J DiSalvo in the 1990s, afforded a variety of single crystals of nitrides. Furthermore, it led to the discovery of a variety of unique crystalline structures to enrich nitride chemistry.^{12,13} This method was also recognized as a single-crystal growth method for technologically important GaN semiconductors¹⁴ and expanded the synthesis of novel intermetallics and silicides.¹⁵

Although considerable efforts have been made to synthesize nitrides, their synthesis requires further improvement, often necessitating inert gas, evacuated glass/vessels, or ammonia cylinders, unlike classic oxide synthesis. Previously, we achieved the low-temperature nitridation of oxides and explosive nitridation of chlorides using NaNH₂. However, NaNH₂ was moisture-sensitive and needed to be handled in a glove box.⁵ Various nitrides have been produced using the air-stable dicyandiamide and metal oxides as starting materials.¹⁶ Recently, Lei et al. reported

that the reaction of $\text{Na}_2\text{MoO}_4/\text{Na}_2\text{WO}_4$ with dicyandiamide in an ambient atmosphere enabled the synthesis of molybdenum and tungsten nitrides using a classic setup for oxide synthesis: an alumina crucible and a box furnace.^{17,18} Interestingly, the synthesized product was a nitrogen-rich nitride, formulated as Mo_2N_3 , even in air.¹⁹ The formation of stable byproducts, CO gas, and NaOCN was proposed as the thermodynamic driving force. Therefore, we postulate that the reactions of sodium ternary oxides with dicyandiamide could further expand nitride chemistry.

When synthesizing nitride powders and single crystals using the batch method, optimizing synthesis conditions, such as the starting materials and temperature, requires a large trial-and-error effort. As nitrides can decompose at high temperatures but cannot react at low temperatures, they are often synthesized over a narrow temperature range.^{20,21} Although in situ synchrotron X-ray diffraction (XRD) has been applied to oxides, sulfides, and chlorides,^{22–25} examples of nitride synthesis are limited.^{26–28} This technique is more advantageous than thermogravimetry (TG) and differential thermal analysis (DTA) for directly understanding the phase evolution of reactions, including those with low enthalpy and small mass changes. The problem with the in situ XRD of nitrides is the difficulty in designing equipment using highly active nitrogen sources, such as ammonia gas, at synchrotron radiation facilities and the associated safety concerns. Even when using nitrogen gas flow, the setting requires time and effort. Thus, rapid in situ XRD investigation of the nitridation of oxides remains challenging.

In our previous study, the synthesis using Na_2MoO_4 and dicyandiamide showed that heating the organic compounds in an alumina crucible produces a reducing atmosphere, which suppresses the oxidation of nitrides.¹⁹ We expect that the use of a narrow capillary for synchrotron X-ray diffraction in ambient atmosphere will allow us to achieve similar synthesis conditions at a high heating rate. In this study, we present the efficient exploration of the nitridation reaction via in

situ synchrotron XRD without using an inert gas flow. In situ XRD measurements revealed that sodium 3d metal oxides (NaVO_3 , NaMnO_2 , and NaFeO_2) could be used to produce a variety of nitrides, carbides, and carbodiimide at temperatures above 500 °C. Guided by this screening, we chose the starting materials and temperature for synthesizing various nitrides on a gram scale using a classic setting for oxide synthesis, that is, an alumina crucible and a box furnace, without using an inert atmosphere. Anion-rich vanadium oxynitrides and iron nitrides were synthesized. During the reaction, Fe_3C , FeNCN ,²⁹ and MnNCN ,³⁰ which have been studied as electrode materials,³¹ were synthesized on a gram scale.

2. EXPERIMENTAL SECTION

2.1. Synthesis of sodium ternary oxides

NaVO_3 (Nacalai Tesque, >97.0%), NaCrO_2 (Kojundo Chemical Laboratory Co. Ltd., >99%), NH_4VO_3 (Wako Pure Chemical Industries Ltd., >99.0%), NaHCO_3 (Fujifilm Wako Pure Chemical Corporation, >99.5%), and V_2O_5 (Kishida Chemical Co. Ltd., >99.0%) were commercially available. NaMnO_2 was synthesized by solid-state synthesis.²⁶ Na_2CO_3 (Wako Pure Chemical Industries Ltd., >99.8%) and MnCO_3 were mixed at a molar ratio of 1 : 2, and the mixture was heated at 600 °C for 30 min in an alumina crucible. $\beta\text{-NaFeO}_2$ was synthesized according to a literature procedure.³² In brief, $\beta\text{-NaFeO}_2$ was obtained by mixing Na_2CO_3 and $\alpha\text{-Fe}_2\text{O}_3$ (Kojundo Chemical Laboratory Co. Ltd., >99.9%) at a molar ratio of 1 : 1 to a total amount of 20 g, after which the mixture was heated to 900 °C (5 °C/min) for 16 h in air.

2.2. Nitridation using Dicyandiamide

A previously reported method was used for the nitridation using dicyandiamide $\text{C}_2\text{H}_4\text{N}_4$.¹⁹ The sodium-containing oxide precursor and dicyandiamide were mixed in the ratios listed in Table S1. A few milligrams of the mixture were inserted into a glass capillary (diameter: 0.5 mm) for in situ synchrotron XRD measurements. The mixtures were placed in alumina crucibles with alumina lids and heated at atmospheric pressure in air at the following temperatures and times for each sample: NaVO_3 was heated to 700 °C for 30 min (V-700); NaFeO_2 was heated to 700 °C for 23, 75, and 90 min (Fe-700-23, Fe-700-75, and Fe-700-90, respectively); and NaMnO_2 was heated to 700 °C for 10, 30, and 60 min (Mn-700-10, Mn-700-30, and Mn-700-60, respectively). A photograph of the alumina crucible and box furnace is given in a previous paper.¹⁹ *It is worth noting that this experiment produces harmful gases. Therefore, heating was performed in an electric furnace placed in a fume hood.* Then, the heated material was washed with distilled water, centrifuged, and dried at room temperature (15–25 °C) in a desiccator to obtain the final product.

In situ XRD measurements were performed at BL02B2 (approval number 2024A1635 for NaVO_3 , NaCrO_2 , NaMnO_2 , and NaFeO_2) and BL13XU (approval number 2023A1042 for $\text{NH}_4\text{VO}_3+\text{NaHCO}_3$ and approval number 2023B1669 for V_2O_5) at SPring-8.³³ The heating rate was 50 °C/min, and the wavelengths were 0.4971992, 0.354050, or 0.35769 Å. The crystal structures of the final products with V, Mn, and Fe were determined by XRD using $\text{CuK}\alpha$ radiation (Rigaku, Miniflex600). The amounts of C, H, and N contained in the final products of V, Mn, and Fe were determined by CHN combustion analyses, where the samples were heated in an oxygen atmosphere at approximately 800 °C using JSL MicroCorder (MT-5). The O and N contents of V-700 were determined by ON combustion analyses, heating with a Sn flux in a carbon crucible in a He atmosphere using an O/N analyzer (Horiba, EMGA-620W). X-ray

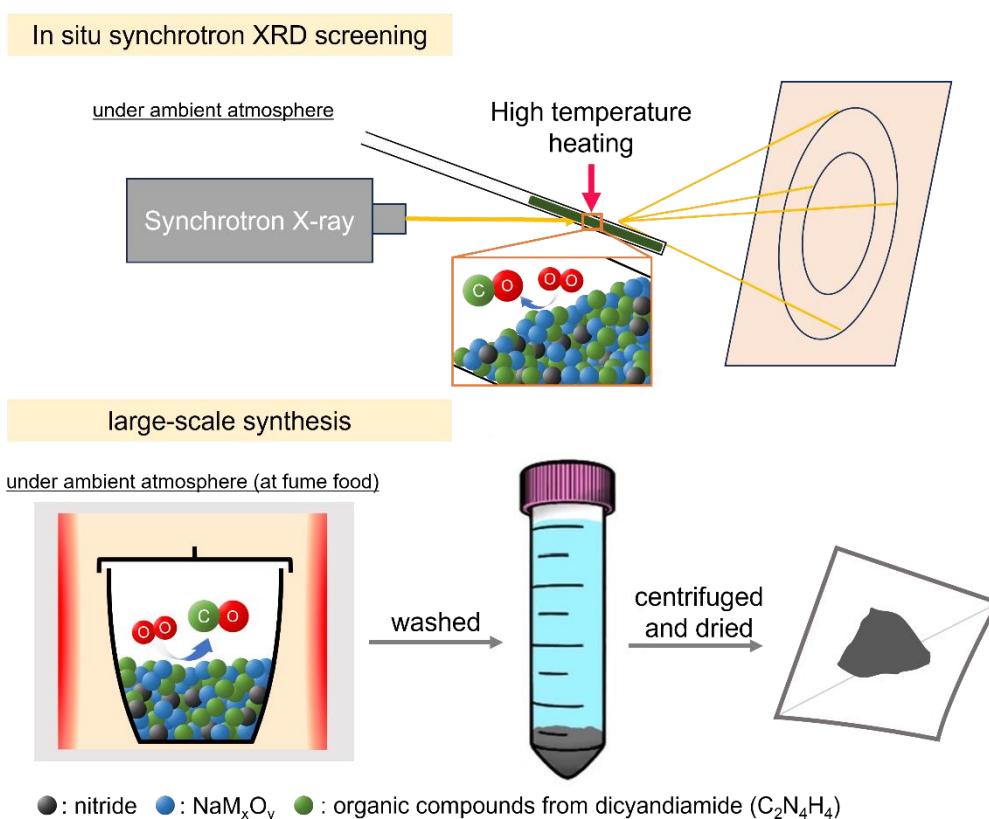
absorption spectroscopy measurements were performed at the V-K edges to investigate the valences of V (V-700). The spectra of the V compounds were recorded at the BL14B2 beamline of SPring-8 (approval number 2023B1576). The magnetic properties of V-700 were measured at 100 *Oe* using a physical property measurement system (Quantum Design PPMS DynaCool) equipped with a vibrating sample magnetometer.

3. RESULTS AND DISCUSSION

3.1. Concept of Screening via In Situ Synchrotron X-Ray Diffraction Measurements and Gram-Scale Synthesis using Classical Ceramic Synthesis

In situ synchrotron XRD measurement was performed at increasing temperatures to investigate the formation of intermediates and nitrides from oxide precursors in the temperature range of 50–750 °C. The experiments were performed on mixtures of sodium-containing oxides and dicyandiamide in a molar ratio of 3 : 5, as shown in Scheme 1. For in situ synchrotron XRD, a few milligrams of the samples were heated using nitrogen gas at one end of a quartz capillary with a diameter of 0.5 mm. One side of the quartz capillary was open, which released the increased pressure owing to the generation of gas species such as CO. The heating rate in this in situ XRD measurement was 50 °C/min, and XRD data were acquired every 11 and 1 s for the BL02B2 and BL13XU beamlines, respectively. Each measurement was completed in approximately 30 min, which included the time required to heat, cool, and change samples. This short-term analysis also allowed the observation of nitridation under a low oxygen pressure before the organic compounds were fully burned out. Therefore, it can be concluded that in situ synchrotron XRD is an efficient analytical method to complete the analysis before the complete combustion of organics and the oxidation during nitridation.

Guided by the reaction temperature determined by in situ synchrotron XRD, a gram-scale synthesis was performed using an alumina crucible covered with a lid and heated in a box furnace without gas cylinders. As described in the introduction section, we believe that in situ synchrotron XRD and the synthesis in the box furnace are not exactly the same in terms of synthesis atmosphere, heat transfer and capacity, and combustion rate of organic compounds. Thus, we used the synthesis temperature determined based on the in situ XRD measurements but changed the synthesis time based on the assumption that different settings affected the synthesis duration. After removing the byproducts by washing, the product was characterized, and subgram-scale samples were available for chemical and structural analyses.



Scheme 1. The concept of rapid nitride synthesis combining in situ synchrotron X-ray diffraction (XRD) and gram-scale synthesis.

3.2. In Situ Synchrotron X-Ray Diffraction Screening of the Nitridation Reaction

3.2.1. In Situ Synchrotron X-Ray Diffraction Screening of Vanadium-based

Compounds

A previous study on the nitridation of molybdenum oxide showed that Na_2MoO_4 produced Mo_2N_3 , while MoO_3 produced a low-crystalline phase and MoO_2 .¹⁹ To understand the effect of sodium on the starting compounds, we performed in situ synchrotron XRD using three different precursors with vanadium oxides, NaVO_3 , V_2O_5 , and a mixture of NH_4VO_3 and NaHCO_3 . NaVO_3 was used as the precursor that contained both sodium and transition metal, V_2O_5 was used as the sodium-free precursor, and the $\text{NH}_4\text{VO}_3+\text{NaHCO}_3$ mixture was used as precursors in which sodium and the transition metal were both present in separate compounds.

Figure 1 shows the in situ synchrotron XRD patterns of the reaction products of these vanadium oxides with dicyandiamide under an ambient atmosphere. In situ synchrotron XRD was performed with different starting materials, and vanadium nitride was identified in all cases above 500 °C. However, above 700 °C, only NaVO_3 produced a single phase of vanadium nitride. The mixture of V_2O_5 produced vanadium nitride, along with V_2O_3 ($C12/c1$), and $\text{NH}_4\text{VO}_3+\text{NaHCO}_3$ produced nitride with V_2O_3 ($R\bar{3}c$) (Figure S1). During the heating of NaVO_3 with dicyandiamide, the valence of the V atom in vanadium oxide decreased from 5 (NaVO_3) to 4.5 (NaV_2O_5) and further to 4.357 ($\text{Na}_9\text{V}_{14}\text{O}_{35}$)³⁴ as the heating temperature increased. This decrease in vanadium valence occurs because dicyandiamide acts as a nitriding and reducing agent.¹⁶

The effect of Na and reaction pathway are discussed based on the comparison between NaVO_3 and V_2O_5 and between NaVO_3 and $\text{NH}_4\text{VO}_3+\text{NaHCO}_3$. When considering the effect of Na by

comparing NaVO_3 and V_2O_5 , NaVO_3 is considered a thermodynamically favorable precursor because of the formation of NaOCN as a thermodynamically stable byproduct, in addition to gas species such as CO and H_2O . Furthermore, the extraction of Na^+ and $1/2\text{O}^{2-}$ from NaVO_3 would increase the surface area of the reactants, which can promote nitridation; Similar nitridation of $\text{Zn}_3\text{V}_2\text{O}_8$ accompanying the phase separation extraction of Zn^{2+} and O^{2-} produces VN with high surface areas.^{35,36} A comparison between the NaVO_3 and $\text{NH}_4\text{VO}_3+\text{NaHCO}_3$ precursors suggests the occurrence of thermodynamically competing reactions to form VN and V-O phases. Although the heating of $\text{NH}_4\text{VO}_3+\text{NaHCO}_3$ produced NaVO_3 , the reaction with the $\text{NH}_4\text{VO}_3+\text{NaHCO}_3$ mixture with dicyandiamide produced vanadium oxides as major phases and VN as minor phases. These results suggest NaVO_3 is a better precursor to lead the reaction to form single-phase VN , not to form V_2O_3 .

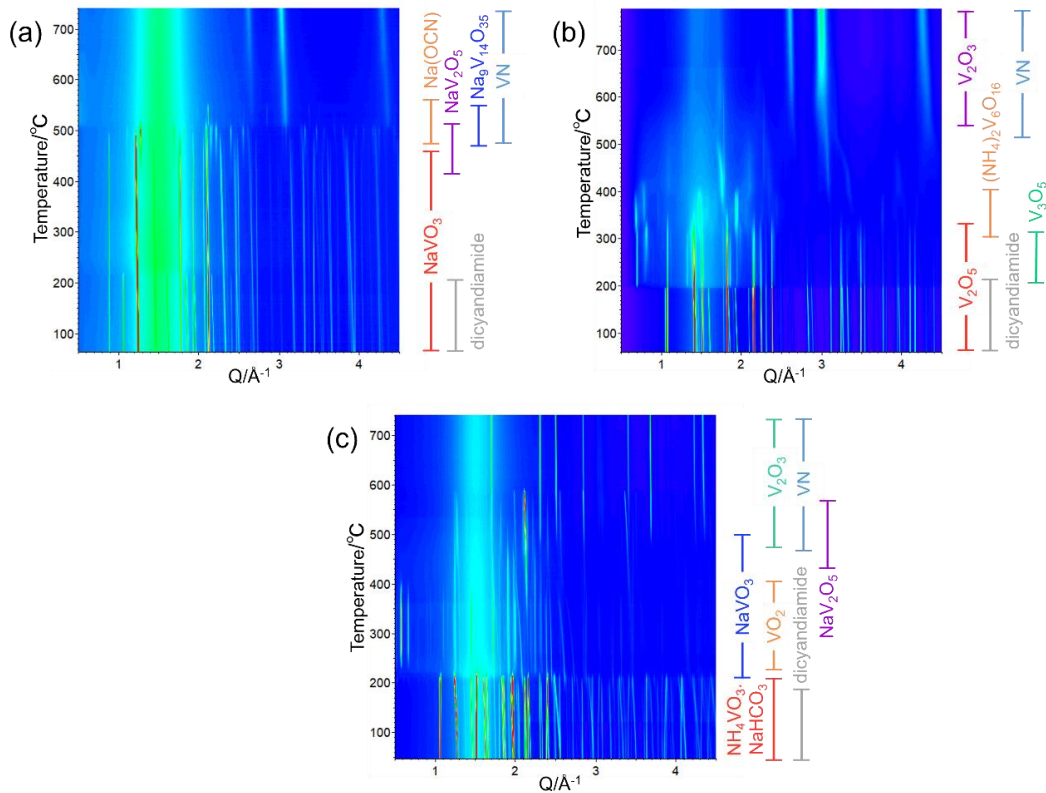


Figure 1. 2D plots of in situ XRD heating of the mixture with vanadium-contained compounds and dicyandiamide at a heating rate of 50 °C/min. (a) NaVO₃ ($\lambda = 0.4971992$ Å), (b) V₂O₅ ($\lambda = 0.35769$ Å), and (c) NH₄VO₃ + NaHCO₃ ($\lambda = 0.354050$ Å). To the right of each plot, crystalline phases that can be indexed are displayed. The halo pattern seen at 1.5 Å⁻¹ is due to the quartz capillary tube used for the measurements.

3.2.2. Nitridation of NaCrO₂, NaFeO₂, and NaMnO₂

In situ synchrotron XRD measurements were performed using different precursors to investigate the effect of sodium on the nitridation of vanadium (Figure 1). The results showed that NaVO₃ was a favorable precursor in the reaction to form a single vanadium nitride phase (Figure 1(a) and 2(a)). For this reason, we chose NaCrO₂, NaFeO₂, and NaMnO₂ as the precursors for other transition metal nitrides.

Figure 2(b) shows the XRD patterns obtained during the reaction of NaCrO₂ with C₂H₄N₄. CrO(OH) was present in the temperature range of 400–600 °C. Unknown products (possibly C₃H₆N₆, melamine) were detected between 250 and 350 °C.³⁷ In addition, CrO(OH) was present above this temperature and could also be synthesized on a gram scale (Figure S2). No nitride formation was observed in this system, partly because of the lower heating temperature compared to that in the formation of CrN using Cr₂O₃ and dicyandiamide under vacuum.¹⁶

For NaFeO₂ (Figure 2(c)), FeNCN, Fe₃O₄, Fe₃N, and Fe₃C were produced upon heating. Furthermore, Figure 2(c) reveals that the crystal phases that emerged exist in the temperature ranges of 450–570, 500–650, 600–710, and 710–790 °C for FeNCN, Fe₃O₄, Fe₃N, and Fe₃C, respectively. In a previous in situ XRD study of sol-gel-derived precursors heated in an ammonia

flow, the reaction proceeded in the following order: Fe_3O_4 , Fe_3N , and Fe_3C .²⁸ In contrast, this study reveals that the reaction using dicyandiamide proceeds via the formation of FeNCN . As shown in Figure 2(c), the Fe_3N peak shifts to the higher-angle side in the range of 600–710 °C with increasing heating temperature. The increase in temperature lowers the lattice parameters (a and c) and the volume of Fe_3N (Figure S3), which cannot be explained by thermal expansion. The nonstoichiometric nature of ε -ion nitrides between Fe_2N and Fe_3N has been reported.³⁸ Thus, this lowering of the lattice parameters accompanies the release of nitrogen gas, possibly from Fe_2N to Fe_3N , which is entropically favorable upon heating.

In the case of the Mn system, MnNCN was formed via the formation of Mn_3O_4 (Figure 2(d)). In addition, it was determined that heating lowered the valence of Mn from 3 for NaMnO_2 ²⁶ to a mixed valence of 2.67 for Mn_3O_4 and 2 for MnNCN ,³⁰ suggesting that dicyandiamide acted as a reducing agent. MnNCN was synthesized in line with the Fe system. However, in contrast to the formation of iron nitrides, no formation of manganese nitrides was observed even at high temperatures. Further investigation is necessary to understand the origin of the high stability of MnNCN compared with FeNCN .

Based on the in situ XRD results, we synthesized vanadium, manganese, and iron nitride/carbodiimide in an alumina crucible in the box furnace under air atmosphere, as described in Section 3.3.

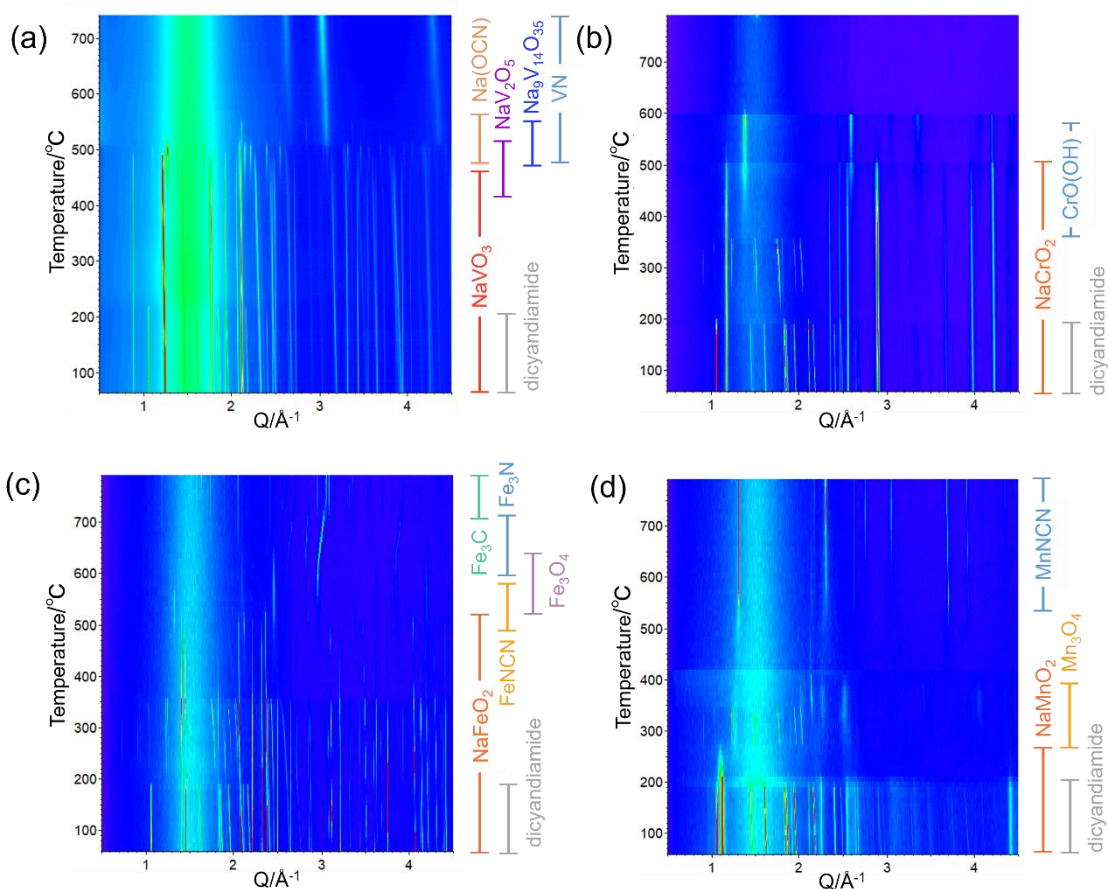


Figure 2. 2D plots of the in situ synchrotron XRD heating of a mixture of sodium-containing 3d transition metal oxides and dicyandiamide at a heating rate of 50 °C/min: (a) NaVO₃ (the same data as Figure 1(a)), (b) NaCrO₂, (c) NaFeO₂, and (d) NaMnO₂. A wavelength of 0.4971992 Å was used (a–d). The halo pattern seen at 1.5 Å⁻¹ is due to the quartz capillary tube used for the measurements.

3.3. Synthesis using a Classical Ceramic Setup

In situ synchrotron XRD revealed that nitrides/carbodiimides/carbides were formed using NaVO₃, NaFeO₂, and NaMnO₂ as precursors. Based on these results, we attempted to synthesize

these compounds on a gram scale under atmospheric pressure for the first time. Table 1 lists the phase and yields of the products.

Table 1. Summary of the phase and yield of the synthesized products in ambient atmosphere.

Sample name	Crystal phase	Amount of final product/g	Yield* /%
V-700	$V_{0.69}N_{0.53}O_{0.47}$ ($Fm\bar{3}m$)	5.6479	84.948
Fe-700-23	FeNCN ($P6_3/mmc$)	1.7127	74.725
Fe-700-75	Fe ₃ N ($P6_322$)	0.4936	34.12
Fe-700-90	Fe ₃ C ($Pnma$)	0.6651	46.48
Mn-700-10	MnNCN ($R\bar{3}m$)	0.9639	42.30
*Metal content assuming the product consists of only the specified crystal phase			
Metal content in precursor			

3.3.1. Vanadium Oxynitride

Because the in situ synchrotron XRD results confirmed the formation of single-phase vanadium nitride above 550 °C, we preliminarily analyzed the products synthesized at 600 and 700 °C for 30 min. Although the XRD patterns of both products were similar (Figure S4), a 2.4 mass% of carbon was detected by CHN combustion analysis in the sample at 600 °C (Table S2). Organic compounds, such as g-C₃N₄, presumably remained at 600 °C.³⁷ Further analysis focused on the sample synthesized at 700 °C (V-700), which contained negligible amounts of carbon residuals (Table S2).

Figure 3 shows the XRD of the final products obtained by heating a mixture of NaVO₃ and dicyandiamide at 700 °C for 30 min under atmospheric pressure, followed by washing and drying. Figure 3 confirms that a cubic rock salt crystalline structure was formed during synthesis

under atmospheric pressure. The lattice parameter ($a = 4.1145(7) \text{ \AA}$) was slightly smaller than that previously reported for VN ($a = 4.13280, 4.138 \text{ \AA}$)^{16,39}, which can be attributed to the different composition of the product synthesized by a different atmosphere because our work utilized an air atmosphere without a tightly closed reaction vessel. Furthermore, the peak intensity ratios differed from those of VN, suggesting that the composition of the product was different from that previously reported. Rietveld refinement (Table 2) indicated that the cation/anion ratio was 0.642(3), suggesting that the obtained products had an anion-rich crystalline structure with cation vacancies, similar to that of Mo_2N_3 .¹⁹

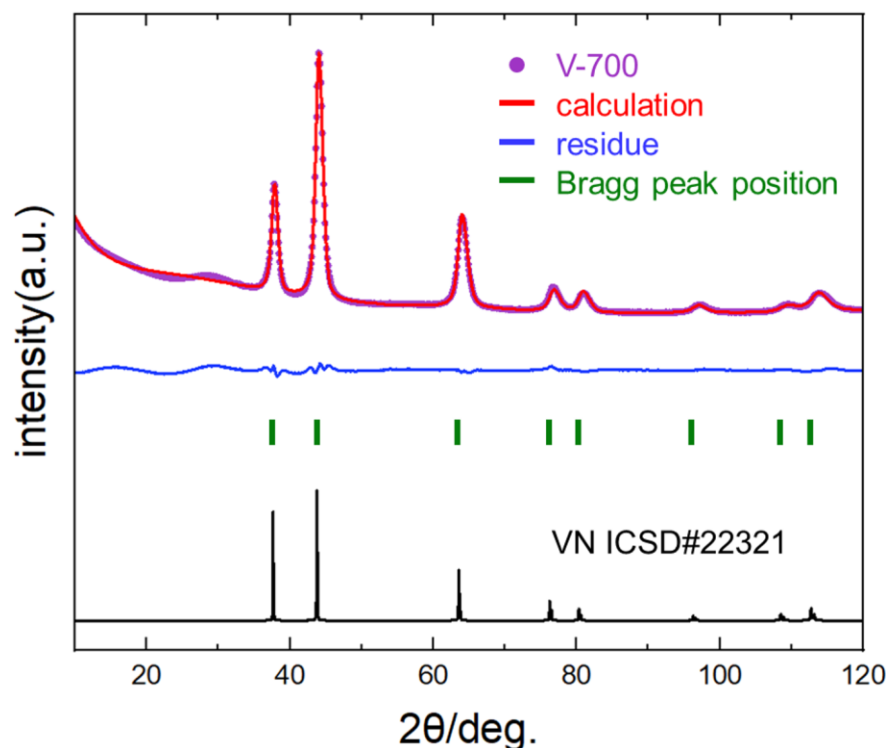


Figure 3. Rietveld profile of vanadium oxynitride synthesized in air. The purple XRD pattern shows the product heated at 700 °C for 30 min. Red and blue lines represent the calculated patterns from the proposed model and residue, respectively. Green ticks are the Bragg peak position. Black line is the calculated pattern of vanadium nitride (ICSD#22321).

Table 2. Rietveld refinement results of V-700

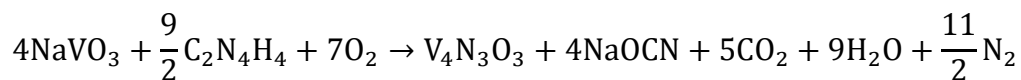
V-700	
<i>a</i>/Å	4.1147(6)
Occ. V	0.642(3)
Occ. N	1
<i>R</i>_{wp}/%	4.31
goodness of fit	0.845

Space group: $Fm\bar{3}m$. The atomic positions of V and N are 0,0,0 and 0, 0, 1/2, respectively. The isotropic displacement parameter, *B*, of V and N is fixed as 1 Å².

Elemental analysis was performed to determine whether the products were nitrides or oxynitrides (Table S2). The C and H contents were analyzed using CHN combustion analysis, and the N and O contents were analyzed using ON combustion analysis. Examination of Na using scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX) revealed that the product contained approximately 3.9 mass%. Assuming that rock salt structure composed of vanadium cation and anion site shared with O²⁻ and N³⁻ and sodium compound exists as an amorphous phase, the cation/anion ratio (V/(N + O)) of rock salt structure was calculated as 0.69. The ratio calculated by the elemental analysis (0.69) was similar to that obtained by the Rietveld analysis (0.642(3)). Accordingly, the product obtained by heating at atmospheric pressure was the anion-rich vanadium oxynitride, V_{0.69}N_{0.53}O_{0.47}. Unfortunately, V has a small

neutron scattering length, making it difficult to perform a more detailed crystal structure analysis of this compound. Neutron diffraction studies using V isotopes may prove the solid solubility of O more precisely.

XRD analysis of the unwashed material confirmed the formation of cubic rock salt vanadium nitride and NaOCN phases (Figure S5). In situ XRD measurements (Fig. 1(a)) confirmed the formation of intermediates $\text{Na}_9\text{V}_{14}\text{O}_{35}$ and NaOCN, whereas ex situ synthesis confirmed the formation of only NaOCN. Thus, NaOCN was produced as a stable byproduct in the synthesis of vanadium nitride in air. Based on the above results, the following reaction is proposed for the synthesis of vanadium nitride at atmospheric pressure using dicyandiamide, assuming O_2 as the oxygen source.



X-ray absorption near edge spectra (XANES) and magnetic measurements indicated that the synthesized oxynitride, V-700, differed from the reported VN. In the XANES spectra of oxynitride, shown in Figure 4(a), the absorption edge shifted toward higher energies, indicating a higher valence than that of VN. This trend was similar to that observed in the XANES study of Mo_2N_3 .¹⁹ No significant diamagnetism of the oxynitride was observed (Figure 4(b)), in contrast to VN, which had a superconducting transition temperature of approximately 9 K.⁴⁰ These results indicated that the electronic structure of V-700 differed from that of the previously reported VN, suggesting that the reaction of NaVO_3 with dicyandiamide produced a new anion-rich vanadium oxynitride.

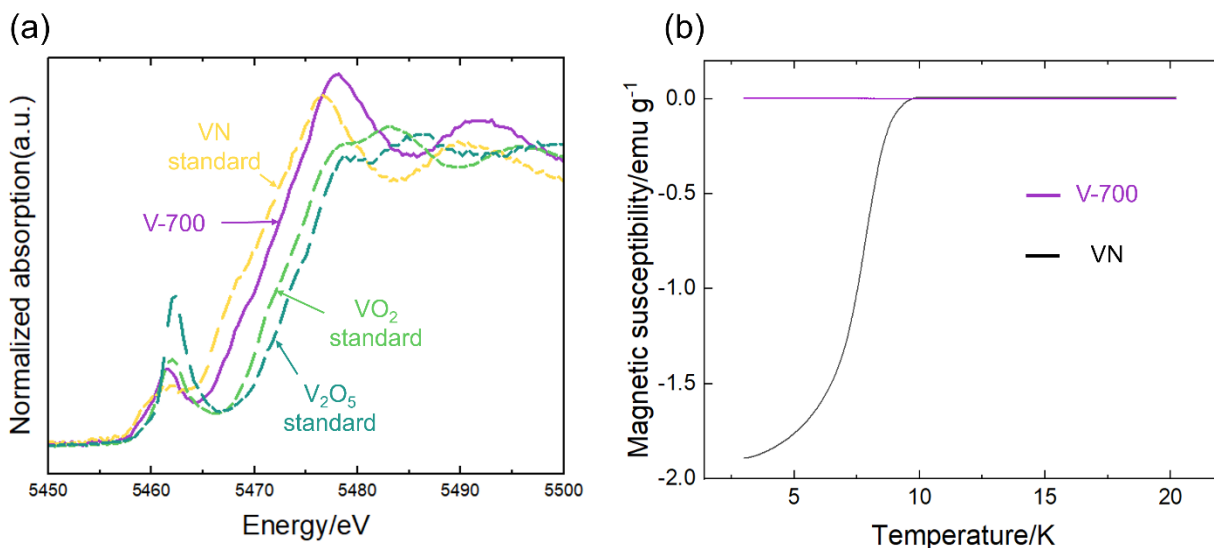


Figure 4. (a) XANES profiles and (b) magnetic susceptibility of vanadium oxynitride synthesized in air (V-700).

3.3.2. Iron Carbodiimide, Nitride, and Carbide

In situ XRD results suggested that the temperature for the synthesis of Fe₃N was 650–710 °C. Therefore, we selected the temperature of 700 °C. Figure 5 shows the XRD patterns of the final product after heating NaFeO₂ and dicyandiamide for 23, 75, and 90 min at atmospheric pressure and washing. The samples synthesized for 23, 75, and 90 min were represented by Fe-700-23, Fe-700-75, and Fe-700-90, respectively. According to XRD analysis, when the starting mixture heated to 700 °C under atmospheric pressure, single-phase FeNCN, Fe₃N, and Fe₃C were synthesized after 23, 75, and 90 min, respectively. Table S3 lists the lattice parameters of FeNCN, Fe₃N, and Fe₃C. The lattice parameters of FeNCN ($a = 3.27913(11)$ and $c = 9.4177(5)$ Å), Fe₃N ($a = 4.71886(15)$ Å, $c = 4.3782(3)$ Å), and Fe₃C ($a = 5.0909(4)$, $b = 6.7424(5)$, and $c = 4.5269(3)$ Å) were close to those reported previously [FeNCN: $a = 3.2689$ and $c = 9.4008$ Å; Fe₃N: $a = 4.69444$ and $c = 4.3739$ Å; Fe₃C: $a = 5.090$, $b = 6.748$, and $c = 4.523$ Å].^{41–43}

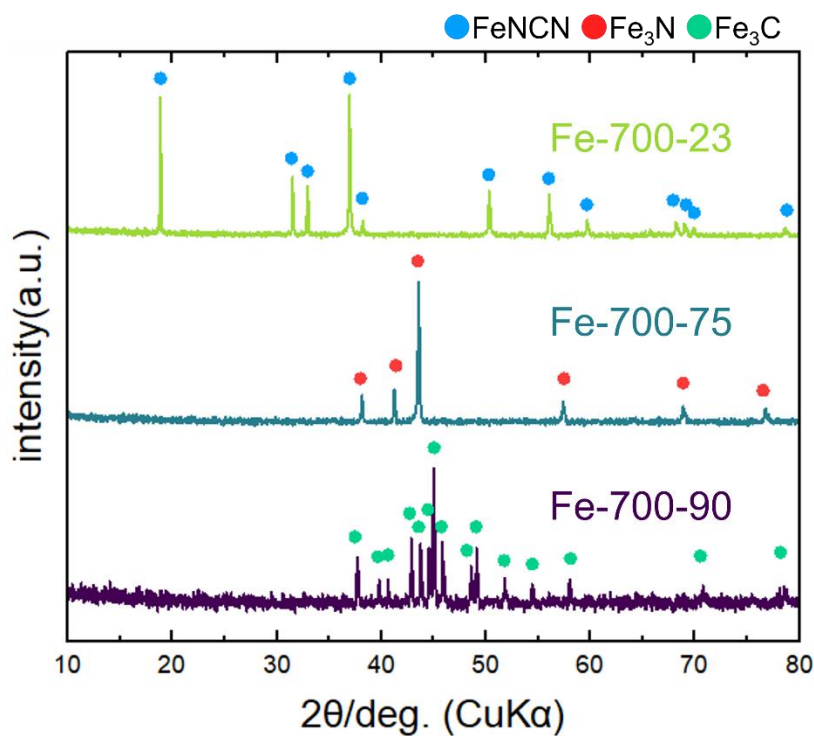


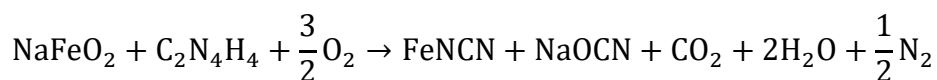
Figure 5. XRD patterns of the final products obtained after heating NaFeO_2 and dicyandiamide at 700 °C for 23, 75 and 90 min.

The CHN analysis results for the Fe-based products are listed in Table S4. The CHN analysis confirmed that residual H atoms in all products were present at a content of 0.17–0.36 mass%, which likely originated from the water or OH/NH species adsorbed on the surface.

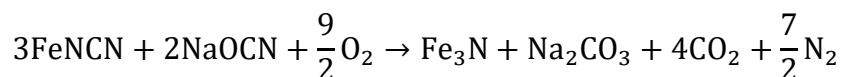
Semiquantitative analysis of the sodium content using SEM-EDS revealed that each sample contained 1.8–3.8 mass% Na. Furthermore, assuming that the only elements present in the product were C, H, N, and Fe, the molar ratios of each substance (Fe : N : C) were calculated as follows: 1 : 2.0 : 0.99 for Fe-700-23, 1 : 0.21 : 0 for Fe-700-75, and 1 : 0.014 : 0.32 for Fe-700-90. The molar ratios of Fe-700-23 and Fe-700-90 were close to the composition ratios of the

products FeNCN and Fe₃C, respectively, whereas iron nitride contained slightly less N, likely because it was partially oxidized, similar to the previously reported composition of Fe₃N.⁴⁴

In this study, when NaFeO₂ and dicyandiamide were heated at atmospheric pressure, the products changed to FeNCN, Fe₃N, and Fe₃C with increasing heating time. The reaction mechanism was further examined by XRD before washing of all products (Figure S6). The formation of FeNCN is accompanied by the formation of NaOCN, suggesting the following reaction. Similar to the formation of vanadium oxynitrides, the thermodynamic driving force to form FeNCN was the production of NaOCN and carbon dioxide.



When iron nitride was formed, not only NaOCN, but also white powder Na₂CO₃ was produced outside the crucible (Figure S6 and S7). The formation of Na₂CO₃ suggests that the evaporation of NaOCN and the formation of CO or CO₂. Although the oxygen pressure is presumably low, the formation of Fe₃O₄, as evident from the in situ XRD analysis, indicates that the existence of oxygen source is reasonable in the reaction.



Before washing, only Fe₃C and unknown peaks were observed for Fe-700-90. It is speculated that iron carbide was produced by the reaction with carbon-containing species or sodium organic salts, which are removed after washing with water.

3.3.3. Manganese Carbodiimide

In situ XRD confirmed the formation of MnNCN at temperatures above 550 °C, and a heating temperature of 700 °C was used to remove residual organic matter. NaMnO₂ was heated with dicyandiamide at atmospheric pressure at 700 °C for 10, 30, and 60 min. After washing and drying, the final products were labeled according to the heating temperature and time as follows: Mn-700-10, Mn-700-30, and Mn-700-60. The XRD patterns of the final products are shown in Figure 6. A single phase of MnNCN was formed when the heating time was 10 min. As the heating time increased, Mn₃O₄ and MnO were formed but not MnN. The lattice parameters of MnNCN (Mn-700-10) were calculated as $a = b = 3.3620(3)$ and $c = 14.3546(13)$ Å, which were close to the reported parameters ($a = b = 3.3583(4)$ and $c = 14.347(2)$ Å).³⁰

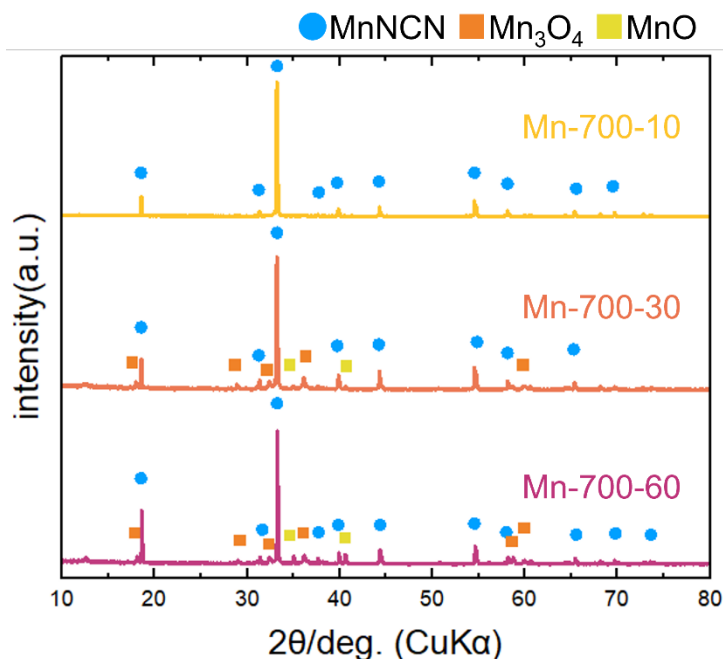


Figure 6. XRD patterns of the products obtained after heating NaMnO₂ and dicyandiamide at 700 °C under atmospheric atmosphere.

Elemental analysis was conducted using SEM-EDX and CHN analyses (Table S5). Na was detected at a concentration of 1.0 wt% using SEM-EDX. The CHN analysis results of Mn-700-10 are listed in Table S5. The molar ratios of Mn, C, and N were determined by elemental analysis in the same way as that for V and Fe. The Mn : N : C ratio was calculated as 1 : 1.6 : 0.82. The N and C ratios were consistent with the composition of MnNCN, but the Mn content was slightly higher than expected. This result can be attributed to the formation of manganese oxides/hydroxides with low crystallinity that is not detected by XRD.

4. CONCLUSIONS

We demonstrated the efficient exploration of the nitridation of various oxides, for which high-throughput in situ measurements have not been performed. In situ synchrotron XRD revealed the advantages of NaVO₃ as a starting material for forming single-phase rock salt vanadium oxynitride and the temperature for synthesizing carbodiimide/nitride/carbide from NaFeO₂ and NaMnO₂. Guided by these rapid screenings, gram-scale oxynitrides, nitrides, carbodiimides, and carbides were successfully synthesized under atmospheric conditions. In situ XRD enabled us to determine the nitridation temperature even for compounds with a narrow synthesis temperature range, such as Fe. Furthermore, by changing the starting material, it was possible to obtain "negative data," which were indicative of conditions under which nitridation did not proceed, thereby providing important clues for selecting an appropriate precursor. Another attractive feature of this method was that, like oxide measurements, it was easy to set up and did not require gas cylinders. Furthermore, data of each sample could be obtained within 30 min. The in situ XRD results obtained in this study showed that sodium ternary oxides underwent nitridation on a gram scale under an ambient atmosphere, in addition to the previously reported Mo and W.^{17,18} It was further revealed that anion-rich vanadium oxynitride could be produced. We

believe that rapid in situ XRD investigation of nitridation will further accelerate nitride chemistry to discover novel functional nitride materials.

ASSOCIATED CONTENT

Supporting Information. A summary of the starting materials, XRD patterns for detailed analysis, and tables for chemical compositions are available.

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BRIEFS

Rapid in situ X-ray diffraction efficiently revealed the nitridation of sodium metal oxides with dicyandiamide to produce various nitrides under an ambient atmosphere.

SYNOPSIS (Word Style “SN_Synopsis_TOC”).

