

Synthetic Route of Layered Titanium Nitride Chloride TiNCl Using Sodium Amide

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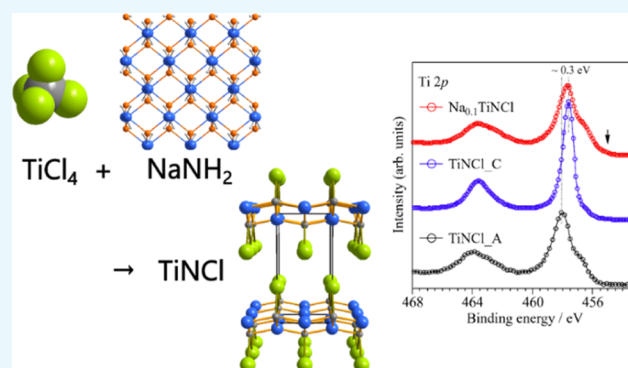


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ABSTRACT: A synthetic route in a closed system for layered titanium nitride chloride TiNCl has been developed using sodium amide NaNH_2 as a nitrogen source. A highly crystalline sample is obtained by an appropriate thermal decomposition of amidated titanium chloride. The obtained TiNCl was also characterized using electronic resistivity measurement and photoemission spectroscopy. TiNCl showed hopping conduction compatible with an in-gap state revealed by photoelectron spectroscopy. However, it appeared highly electron-doped, albeit without showing superconductivity. Comparison with the spectrum of superconducting sodium-doped samples suggests the presence of the microstructure required to exhibit superconductivity.



1. INTRODUCTION

Layer-structured ternary metal nitride halides MNX ($M = \text{Ti}, \text{Zr}, \text{Hf}$; $X = \text{Cl}, \text{Br}, \text{I}$) contain two polymorphs, the α -form and β -form, with different metal nitride networks.¹ Both are band insulators and are changed into superconductors with moderately high transition temperatures upon electron doping. It is well known that lithium-intercalated β -form HfNCl is a superconductor with a transition temperature T_c as high as ~ 26 K.^{1–3} The superconductivity in the β -form compounds has been studied extensively. The mechanism reported is not easy to interpret all the experimental results consistently by a conventional phonon-mediated Bardeen Cooper Schrieffer mechanism.^{4–7}

On the other hand, the α -form compound, TiNCl, also shows superconductivity at $T_c \sim 16$ K after electron doping by intercalating alkali or alkaline earth metals and/or organic bases.^{8–10} The importance of interlayer coupling was reported for pairing;^{11,12} the superconducting characteristics are significantly different from the β -type. A comparison of the superconductivity in different M -N networks will be interesting.

In a study on a superconducting mechanism, the isotope effect on T_c provides crucial evidence of whether electron–phonon interaction is responsible for the superconductivity. However, synthesizing TiNCl has several issues that hinder the investigation of the effect. TiNCl is easily hydrogen-reduced and decomposed into TiN at a temperature ranging from 400 to 450 °C.¹³ In addition, it cannot be obtained by the reaction within a sealed metal or metal hydrides with NH_4Cl because TiH_2 is stably formed at 400 °C, unlike the other layered

nitride halides such as Zr/HfNCl .^{1,2} Then, TiNCl was conventionally prepared by the thermal decomposition of TiCl_4 under NH_3 gas flow in an open system with a vertical reaction cell,^{8,14} but retaining the ^{15}N isotope using NH_3 gas as a nitrogen source is extremely difficult or almost impossible realistically.

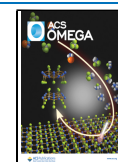
In a conventional reaction, large amounts of intermediates such as titanium amides, NH_4Cl , and $(\text{NH}_4)_2\text{TiCl}_6$ are produced with an intense exothermic reaction. These intermediates are gradually heated up to 400 °C under the NH_3 stream and maintained at that temperature for several hours to purge the excess compounds; a low crystalline TiNCl precursor is left at the bottom of the reaction cell. The precursor is sealed together with a small amount of the transporting agent NH_4Cl and then purified by chemical vapor transport as highly crystalline TiNCl.⁸

Considering the above synthesis process, if the TiNCl precursor could be formed using a solid reagent other than gaseous NH_3 as a nitrogen source in a closed reaction cell, an essential technique for synthesizing ^{15}N substituents would be developed. It could help not only to elucidate the superconducting mechanism of TiNCl but also to investigate the isotopic effect of other metal nitride superconductors.

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NaNH_2 is a highly reactive solid nitrogen source used for the combustion reaction with 3d transition-metal chlorides to obtain metal nitrides.^{15,16} The reactions are thermodynamically driven by a metathesis reaction involving the formation of stable NaCl. NaCl does not contribute to chemical transport; if the reaction with TiCl_4 can be controlled, TiNCl may be obtained in a sealed glass tube. In this study, a synthetic route for highly crystalline TiNCl has been developed using NaNH_2 in a sealed Pyrex glass tube without an NH_3 gas stream. The chemical state of such obtained semiconducting TiNCl was characterized using photoemission spectroscopy and compared with conventionally obtained TiNCl .

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. TiCl_4 (Aldrich, >99.0%) and NaNH_2 (Wako, 90.0+%) were mixed under dry nitrogen gas flow and then sealed into an evacuated glass tube. Vacuum sealing was performed by freezing the sample part with liquid nitrogen to prevent the volatilization of TiCl_4 . *Caution!* An intense exothermic reaction occurs when these reagents are mixed. Synthesis using a large amount of the starting materials may cause a severe accident with an explosive reaction. The typical amount of TiCl_4 and NaNH_2 used was about 2 mL and 0.2 g, respectively, using a glass tube with an inner diameter of 8 and 200 mm in length. There is a risk of explosion of HCl and NH_3 gases during release. Wear protective glasses during the experiment.

2.2. Characterization. The infrared (IR) spectrum was measured by a KBr disk using a Shimadzu IRAffinity-1 spectrometer. Thermogravimetric analysis was performed by maintaining the temperature at each value for 15 min while evacuating and then taking it out from the reaction cell while flowing dry nitrogen gas and measuring the mass. Heating was performed at a heating rate to reach the target temperature within a few minutes. Powder X-ray diffraction (XRD) measurements were carried out using an imaging plate Guinier camera (Huber, model 670G) with $\text{Mo K}\alpha_1$ radiation ($\lambda = 0.709260 \text{ \AA}$) and a rotating goniometer, where the sample was sealed in a thin Pyrex glass capillary. A TOPAS-Academic software package was used for the Rietveld analysis.¹⁷ A backscattered electron (BSE) image and the energy-dispersive X-ray spectra were observed using a scanning electron microscope (JEOL, JSM-6010LA). Electrical resistance was measured by an electrode-insertion type diamond anvil cell used as a resistance detector for microcrystals.¹⁸ Magnetic susceptibility was measured using a superconducting quantum interference device magnetometer (Quantum Design) under zero-field cooling and field cooling with an applied magnetic field of 10 Oe.

Hard X-ray photoelectron spectroscopy (HAXPES) measurements were performed at the beamline 47XU of SPring-8 at room temperature with $h\nu = 7.94 \text{ keV}$ photons, and the total energy resolution was set to 0.25 eV.^{19,20} All samples were transported to the equipment without exposure to air, and then they were fractured under a pressure of 10^{-6} Pa to obtain a clean surface. The binding energy was calibrated using the Fermi edge of Au.

3. RESULTS AND DISCUSSION

3.1. Synthesis of TiNCl Using NaNH_2 . **3.1.1. Preliminary Reaction of TiCl_4 with NaNH_2 .** The sealed glass tube containing TiCl_4 and NaNH_2 was gradually heated up to

$150 \text{ }^\circ\text{C}$ for 12 h and then kept at this temperature for 1–2 days. Prolonged heating was found to be favorable to the reaction. It is essential to react sufficiently at a lower temperature than $200 \text{ }^\circ\text{C}$ to prevent the volatilization of TiCl_4 and the explosion of the glass tube. Hereafter, the resulting solid is called the preliminary reacted solid.

3.1.2. Direct Heating of the Preliminary Reacted Solids. The preliminary reacted solid was directly heated around $400 \text{ }^\circ\text{C}$ in the as-sealed form. The heating treatment did not result in TiNCl , but $(\text{NH}_4)_2\text{TiCl}_6$ and low crystalline TiN were recovered instead. It showed the same result as with the chemical transport. The existence of $(\text{NH}_4)_2\text{TiCl}_6$ indicates that the remaining TiCl_4 has reacted with NH_4Cl upon further heating NH_4Cl . NH_4Cl can be produced by the reaction of TiCl_4 and NH_3 emitted by the decomposition of NaNH_2 .

On the other hand, the production of TiN suggests that a Ti-NH_2 bond replaced at least one Ti-Cl bond in TiCl_4 ; possibly, a titanium amide chloride such as $\text{TiCl}_3(\text{NH}_2)$ is generated before the heating process. This TiCl_4 ammonolysis reaction is energetically favorable.^{21,22} TiCl_4 forms ammonia-incorporated complexes with the $\text{TiCl}_4 \cdot x\text{NH}_3$ gross composition, and heating the complexes in an ammonia-rich atmosphere results in the stepwise amination of TiCl_4 to finally form $\text{TiCl}(\text{NH}_2)_3$.^{13,23,24}

3.1.3. IR Study of the Preliminary Reacted Solids. The IR spectrum of the preliminary reacted solids was measured to examine the reaction of TiCl_4 with NaNH_2 , as shown in Figure 1. Three prominent absorption bands were observed in the

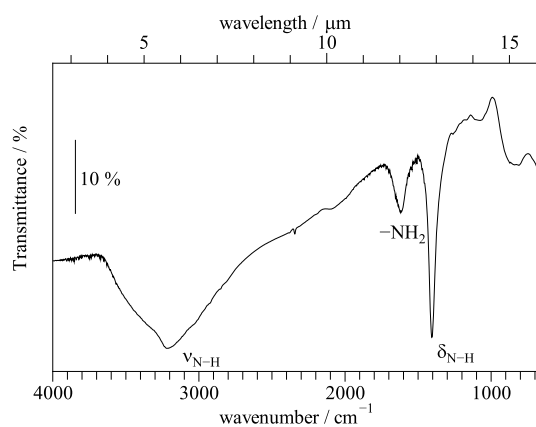


Figure 1. IR spectrum for the TiCl_4 and NaNH_2 mixture after heating at $150 \text{ }^\circ\text{C}$.

spectrum. The frequencies around 3200 and 1400 cm^{-1} are close to those of vibrational modes of NH_4^+ and/or NH_3 stretching of the ammine complexes; then, they were assigned to N-H stretching and N-H deformation vibrations, respectively.²⁵ The XRD measurement of the same solid shows a mixture pattern of NaCl and other unknown phases with relatively broad peaks, but no NH_4Cl has been observed. This finding indicates that the absorption bands are attributed to the ammonia complexes of titanium chloride, such as $\text{TiCl}_4 \cdot x\text{NH}_3$.²⁶

One more IR absorption band could be assigned to the $-\text{NH}_2$ groups, which has been reported to appear at a frequency of 1550 cm^{-1} .^{26–28} It has been reported that the heating of the ammonia complexes $\text{TiCl}_4 \cdot x\text{NH}_3$ gradually decreases its ammonia content and results in the stepwise amination of TiCl_4 .²⁶ It is reasonable that the preliminary

reacted solids contain $\text{TiCl}_3(\text{NH}_2)$, $\text{TiCl}_2(\text{NH}_2)_2$, and $\text{TiCl}(\text{NH}_2)_3$, together with $\text{TiCl}_4 \cdot x\text{NH}_3$. Namely, the reaction at this process can be written as the equation $\text{TiCl}_4 + \text{NaNH}_2 \rightarrow \text{TiCl}_3(\text{NH}_2) + \text{NaCl}$ in the simplest case.

3.1.4. Thermogravimetric Study of the Preliminary Reacted Solids. As expected in the zirconium analogue, the amide $\text{TiCl}_3(\text{NH}_2)$ would thermally decompose into TiNCl .²⁹ Since TiNCl was not transported from the as-obtained mixture described in Section 3.1.2, some reaction factors impede the chemical transport at around 400 °C. Thermogravimetric analysis while evacuating was performed on the preliminary reacted solids, as shown in Figure 2. On evacuation up to 180

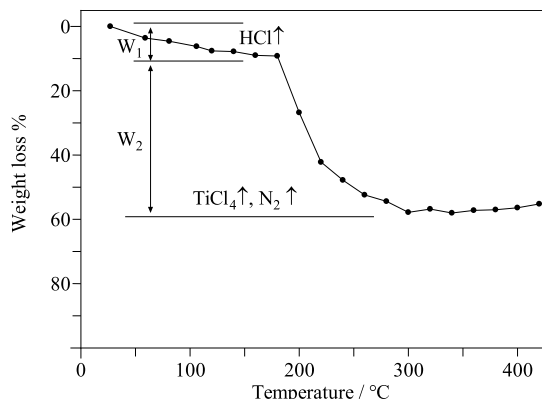


Figure 2. Thermogravimetric curve for the preliminary reacted solids measured in vacuum.

°C, the solids lost their weight gradually. The initial state comprises aminated TiCl_4 , NaCl , $\text{TiCl}_4 \cdot x\text{NH}_3$, and a small amount of unreacted NaNH_2 . In the literature of ref 26, $\text{TiCl}_4 \cdot x\text{NH}_3$ (most stably $x = 8$) releases its ammonia content to the minimum $x = 2$ in the vacuum treatment even at room temperature. NaNH_2 shows a slight N_2 emission below 230 °C.³⁰ The weight reduction factor below 180 °C in this study is mainly attributed to the aminated TiCl_4 decomposition. The simplest reaction in this stage can be written as an equation



The weight loss for this reaction was calculated to be 32%. It should be increased if the stepwise amination has much proceeded according to the following equations



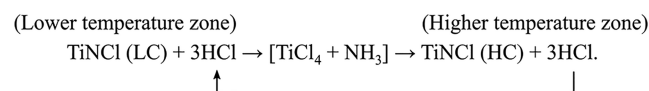
and so forth. However, the actual weight loss W_1 was only 9.2%. This result indicates that the reaction had not completed at this temperature but would continue to a much higher temperature.

The second decomposition stage, accompanied by a steep weight loss beginning from 180 °C, has been observed up to 300 °C, and the decomposition seems to complete at this temperature. A similar thermogravimetric curve for the zirconium analogue was observed in the literature, and the following equation was proposed: $2\text{ZrCl}_3(\text{NH}_2) \rightarrow \text{ZrNCl} + \text{ZrCl}_4 + \text{NH}_4\text{Cl}$.²⁹ On further heating up to 800 °C, the sample was decomposed to ZrN . In the present study, the decomposition temperature of TiNCl can be considerably lower than that of ZrNCl , especially if the unreacted NaNH_2 exists as an even stronger reducing reagent. Then, the

following reaction would have simultaneously occurred with reaction 1 above 200 °C; $8\text{TiNCl} \rightarrow 2\text{TiCl}_4 + 6\text{TiN} + \text{N}_2$. The weight loss for this reaction was calculated to be 52%. Although this value is in good agreement with the amount of the loss W_2 (49%), the quantitative analysis of this stage is much more complicated since reactions 2 and 3 should have occurred in parallel under the evacuation condition, which resulted in a significant weight loss.

3.1.5. Procedures to Obtain TiNCl . From these results, while the preliminary reacted solids include Ti-NH_2 bonds, they contain unreacted TiCl_4 and other ammonia complexes of TiCl_4 . The procedures to obtain TiNCl using NaNH_2 can be proposed as follows. (1) The sealed mixture of $\text{TiCl}_4 + \text{NaNH}_2$ sufficiently reacts around 160 °C to obtain preliminary reacted solids. (2) The seal is opened, and unreacted TiCl_4 is purged from the glass tube. Then, the preliminary reacted solids are evacuated again with an elevated temperature of 180 °C to remove HCl from $\text{TiCl}_3(\text{NH}_2)$ and/or other aminated compounds. Here, we can obtain a low-crystallinity (LC) TiNCl with the whole equation in the simplest case written in $\text{TiCl}_4 + \text{NaNH}_2 \rightarrow \text{TiCl}_3(\text{NH}_2) + \text{NaCl} \rightarrow \text{TiNCl} + \text{NaCl} + 2\text{HCl}$. (3) The heating and evacuation should be stopped before decomposition to TiN occurs and sealed again into a glass tube. (4) The glass tube sends chemical transport to obtain highly crystalline (HC) TiNCl .

3.1.6. Chemical Vapor Transport of TiNCl . The following equation can simply describe the net chemical transport



HCl is required to decompose LC TiNCl into a gas. Since the reactions in formula 1 and 2 would still occur in parallel, the transport reaction will proceed simply by sealing the resulting LC- TiNCl -containing materials as they are. A small amount of NH_4Cl may be added as a transport agent. The transport reaction occurs in the higher-temperature zone. When the glass tube was put into a horizontal furnace at a temperature gradient of 400–230 °C, the purified and highly-crystalline (HC) TiNCl was successfully obtained, as shown in the XRD pattern of Figure 3 and the BSE image of Figure S1. The crystallographic parameters were refined within a single

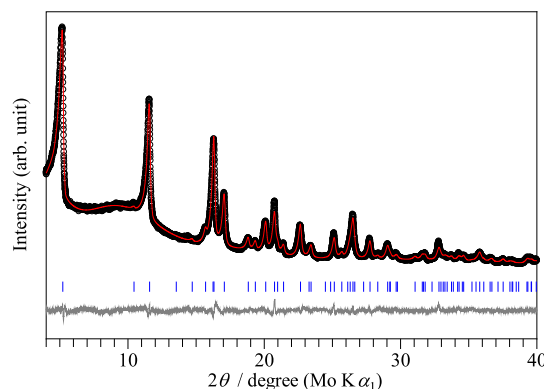


Figure 3. Rietveld analysis of the XRD pattern of TiNCl obtained in the process proposed in this study. Open circles show the observed data points, and the solid line represents the calculated diffraction pattern. The tip marks are the calculated 2θ angles for the Bragg peaks of TiNCl .

phase of TiNCl and agreed with the previously reported value.⁸ The details are compared with conventionally obtained TiNCl, as shown in Table S1. The parameters are almost the same, but a slight difference can be seen in the bonding distances in Ti–N and Ti–Cl, attributed to the difference in the coordinating position of the N atom. It may be affected by factors apart from the elements composed of the compound, such as hydrogen found in ZrNCl.³¹ Note that the temperature on the lower side should be less than 250 °C, which is significantly lower than the regular chemical transport of TiNCl.⁸ If this becomes too high, the transport fails with an explosive reaction, resulting in all the compounds in the glass tube becoming soot-like. The reaction is probably due to the combustion reaction induced by the remaining unreacted NaNH₂.¹⁵ In order to suppress this reaction, it is essential to keep a low temperature of about 230 °C in the lower-temperature zone.

3.2. Characterization of the Obtained TiNCl. The electrical property of the obtained semiconductor TiNCl (TiNCl_A) was evaluated. The transport characteristics were evaluated and compared with the conventionally synthesized TiNCl (TiNCl_C). Both samples show metallic-like conduction only near room temperature, and the electrical resistance increases as the temperature decreases below 270 K (Figure S2). This behavior is close to the semiconducting nature expected from ideal band calculation results.⁸ The temperature dependence of resistance of TiNCl_A is closer to hopping conduction,³² suggesting an in-gap state near the Fermi level (E_F). This finding infers some impurities around N atoms, and the X-ray structural analysis supports it.

HAXPES was used to elucidate the chemical state of TiNCl_A compared with TiNCl_C. This measurement indicates the following three things. First, the top of the valence band of TiNCl_A lies at ~1.5 eV, comparable to the previously reported value (Figure S3).³³ There is a tiny intensity at the E_F , appearing as a localized state. This fact is compatible with the semiconductor-like properties of hopping conduction suggested by the resistivity measurement.

Second, the Ti 2*p* HAXPES spectrum consists of two peaks at around 457.5 and 463.5 eV, corresponding to the spin–orbit split of Ti 2*p*_{3/2} and Ti 2*p*_{1/2}, respectively, as shown in Figure 4a. The Ti 2*p*_{3/2} peak has a broad shoulder-like component in the lower binding energy side, similar to the valence splitting of previously reported electron-doped samples.^{33,34}

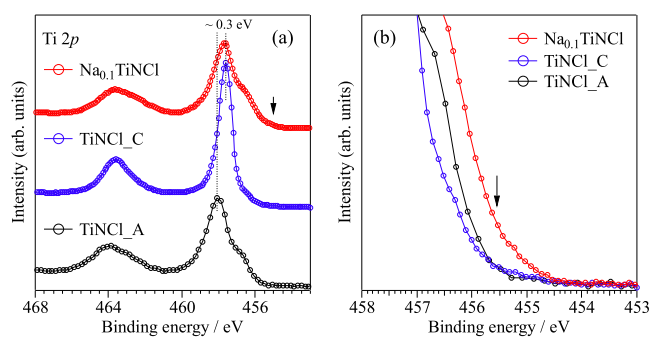


Figure 4. (a) Ti 2*p* core-level spectra of TiNCl obtained in this study (TiNCl_A) compared with that obtained using the conventional method (TiNCl_C) together with intercalated samples (Na_{0.1}TiNCl). Each spectrum was normalized by the area of the peak. (b) Enlargement of the fine structure around 455.5 eV.

Third, the prominent peaks of TiNCl_A shift to the higher binding energy side about 0.3 eV compared to TiNCl_C, even though the sample was not a Na-doped one. The same chemical shift is also observed in the core-level spectrum of the other elements N 1*s* and Cl 2*p* (Figure S4). These three findings suggest that TiNCl_A seems to be highly electron-doped. Surprisingly, the peak shape of TiNCl_A is quite similar to sodium-intercalated TiNCl prepared from the conventional way (denoted as Na_{0.1}TiNCl) when the peaks shifted 0.3 eV to the higher binding energy side. The intercalation compound Na_{0.1}TiNCl shows superconductivity around 16 K; however, TiNCl_A did not show any specific magnetic signals down to 1.8 K unless intercalated (Figure S5). This result suggests an essential difference in the electronic structure of TiNCl_A and Na_{0.1}TiNCl.

Carefully comparing the core-level spectrum of Ti 2*p* of these samples, another fine structure around 455.5 eV (indicated by arrows in Figure 4b) emerges other than the shoulder-like component of the main structure of Na_{0.1}TiNCl. Although the area of the fine structure is small, peak fitting can be performed reliably, as shown in Figure 5. We can see a small contribution of component D in the peak fitting of Na_{0.1}TiNCl. However, it could not be observed in pristine TiNCl_A despite its highly electron-doped state. It did not appear unless the sample was Na-doped (Figure 5b).

On the other hand, the structure around 457 eV (denoted as component A) mainly corresponds to the amount of Ti³⁺ content in the sample. Since the electron doping should increase the Ti³⁺ content, component A was found in TiNCl_A and TiNCl_C even in the pristine compound, and it increased monotonically with the Na concentration. Considering that all Na-doped samples exhibit superconductivity, it is very plausible that component D is necessary for the appearance of superconductivity. This finding is essential to clarify the electronic state required for superconductivity for this group of materials. Further precise measurements and theoretical studies are required.

However, it is still unclear why such highly electron-doped TiNCl was obtained. It is reasonable that it is due to a property peculiar to the synthetic route in this study, namely, the usage of NaNH₂. Some unreacted NaNH₂ remaining in the reaction cell may cause another reaction besides the proposed ideal reactions. The decomposition of NaNH₂ alone hardly occurs at 230 °C, but the reaction can proceed even at a lower temperature at the most reactive interface of the solids in contact. This reaction would release NaH, NH₃, H₂, and N₂, as the intermediate product.³⁰ There is another report that adding NaH to NaNH₂ suppresses the generation of ammonia and release H₂.³⁵ The partial pressure of NH₃ is suppressed in the decomposition process, and the reaction may occur in the presence of H₂ or N₂ gas instead. It might cause hydrogen incorporation into the obtained TiNCl. In ZrNCl, it has been reported that the incorporated hydrogen atoms sit around N atoms with a suggestion of carrier number change.³¹ The same intercalation might happen in TiNCl, bringing a slight difference in the coordinating position of N atoms, and may influence the carrier number, resulting in high electron doping. This side reaction is not easy to control, and these complicated reaction processes may be a factor that give an electronic state different from that of TiNCl obtained by the conventional method. It is suggested that the atmosphere during chemical transport strongly affects the quality of the sample. The other

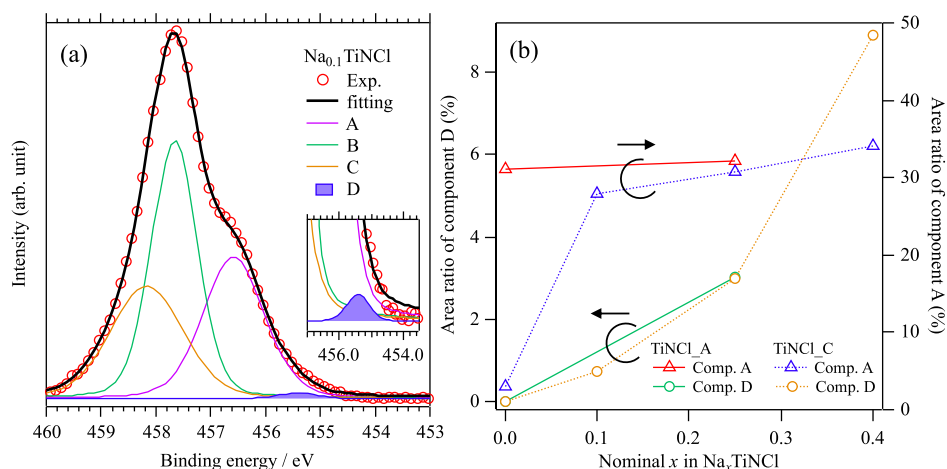


Figure 5. (a) Result of peak fitting of Ti 2p HAXPES spectra in $\text{Na}_{0.1}\text{TiNCl}$ obtained from TiNCl_C . The inset is an enlargement scale of component D. (b) Nominal Na amount dependence of the area ratio of component A and D to the other components compared with TiNCl_A and TiNCl_C .

sample morphology-dependent functionalities might also be expected in the present pristine TiNCl .

4. CONCLUSIONS

We prepared a HC TiNCl using a reaction of TiCl_4 with NaNH_2 in a closed system. This report is the first example of synthesizing TiNCl in a closed system, which requires high-level technical skills to synthesize even by conventional methods. This technique can maintain the initial nitrogen source and is necessary to investigate the ^{15}N isotope effect for elucidating the superconducting mechanism. It could be carried out not only for TiNCl but also for the other metal nitride superconductors. Furthermore, the obtained TiNCl appeared highly electron-doped, albeit without showing superconductivity. Comparison with the spectrum of superconducting sodium-doped samples suggests the presence of a microstructure required to exhibit superconductivity. It may be a clue to elucidate the mechanism of superconductivity, which has been unsolved for more than 10 years since it was discovered in 2009.⁸

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c06986>.

Details of crystallographic parameters and additional experimental results, including a typical image of the sample crystals (PDF)

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Notes

The authors declare no competing financial interest.

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