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著者	Tanaka Masashi, Kataoka Noriyuki, Matsumoto Ryo, Inumaru Kei, Takano Yoshihiko, Yokoya Takayoshi, Yoshihiko Takano
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# Synthetic Route of Layered Titanium Nitride Chloride TiNCl Using Sodium Amide

Masashi Tanaka,<sup>\*,#</sup> Noriyuki Kataoka,<sup>#</sup> Ryo Matsumoto, Kei Inumaru, Yoshihiko Takano, and Takayoshi Yokoya



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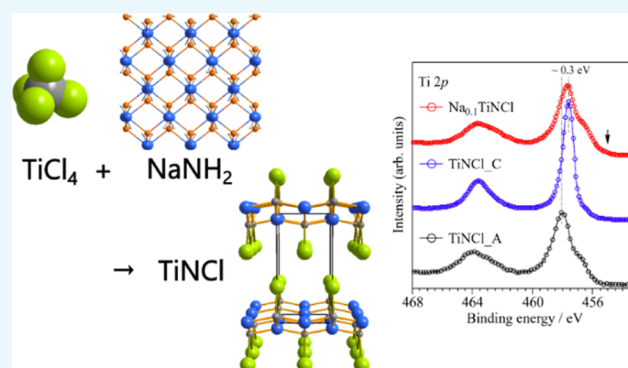


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Supporting Information

**ABSTRACT:** A synthetic route in a closed system for layered titanium nitride chloride TiNCl has been developed using sodium amide  $\text{NaNH}_2$  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  $\text{MNX}$  ( $M = \text{Ti}, \text{Zr}, \text{Hf}$ ;  $X = \text{Cl}, \text{Br}, \text{I}$ ) contain two polymorphs, the  $\alpha$ -form and  $\beta$ -form, with different metal nitride networks.<sup>1</sup> Both are band insulators and are changed into superconductors with moderately high transition temperatures upon electron doping. It is well known that lithium-intercalated  $\beta$ -form  $\text{HfNCl}$  is a superconductor with a transition temperature  $T_c$  as high as  $\sim 26$  K.<sup>1–3</sup> The superconductivity in the  $\beta$ -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.<sup>4–7</sup>

On the other hand, the  $\alpha$ -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.<sup>8–10</sup> The importance of interlayer coupling was reported for pairing;<sup>11,12</sup> the superconducting characteristics are significantly different from the  $\beta$ -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.<sup>13</sup> In addition, it cannot be obtained by the reaction within a sealed metal or metal hydrides with  $\text{NH}_4\text{Cl}$  because  $\text{TiH}_2$  is stably formed at 400 °C, unlike the other layered

nitride halides such as  $\text{Zr}/\text{HfNCl}$ .<sup>1,2</sup> Then, TiNCl was conventionally prepared by the thermal decomposition of  $\text{TiCl}_4$  under  $\text{NH}_3$  gas flow in an open system with a vertical reaction cell,<sup>8,14</sup> but retaining the  $^{15}\text{N}$  isotope using  $\text{NH}_3$  gas as a nitrogen source is extremely difficult or almost impossible realistically.

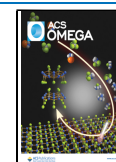
In a conventional reaction, large amounts of intermediates such as titanium amides,  $\text{NH}_4\text{Cl}$ , and  $(\text{NH}_4)_2\text{TiCl}_6$  are produced with an intense exothermic reaction. These intermediates are gradually heated up to 400 °C under the  $\text{NH}_3$  stream and maintained at 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  $\text{NH}_4\text{Cl}$  and then purified by chemical vapor transport as highly crystalline TiNCl.<sup>8</sup>

Considering the above synthesis process, if the TiNCl precursor could be formed using a solid reagent other than gaseous  $\text{NH}_3$  as a nitrogen source in a closed reaction cell, an essential technique for synthesizing  $^{15}\text{N}$  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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$\text{NaNH}_2$  is a highly reactive solid nitrogen source used for the combustion reaction with 3d transition-metal chlorides to obtain metal nitrides.<sup>15,16</sup> 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  $\text{TiCl}_4$  can be controlled,  $\text{TiNCl}$  may be obtained in a sealed glass tube. In this study, a synthetic route for highly crystalline  $\text{TiNCl}$  has been developed using  $\text{NaNH}_2$  in a sealed Pyrex glass tube without an  $\text{NH}_3$  gas stream. The chemical state of such obtained semiconducting  $\text{TiNCl}$  was characterized using photoemission spectroscopy and compared with conventionally obtained  $\text{TiNCl}$ .

## 2. EXPERIMENTAL SECTION

**2.1. Sample Preparation.**  $\text{TiCl}_4$  (Aldrich, >99.0%) and  $\text{NaNH}_2$  (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  $\text{TiCl}_4$ . *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  $\text{TiCl}_4$  and  $\text{NaNH}_2$  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  $\text{NH}_3$  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.<sup>17</sup> 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.<sup>18</sup> 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.<sup>19,20</sup> All samples were transported to the equipment without exposure to air, and then they were fractured under a pressure of  $10^{-6} \text{ Pa}$  to obtain a clean surface. The binding energy was calibrated using the Fermi edge of Au.

## 3. RESULTS AND DISCUSSION

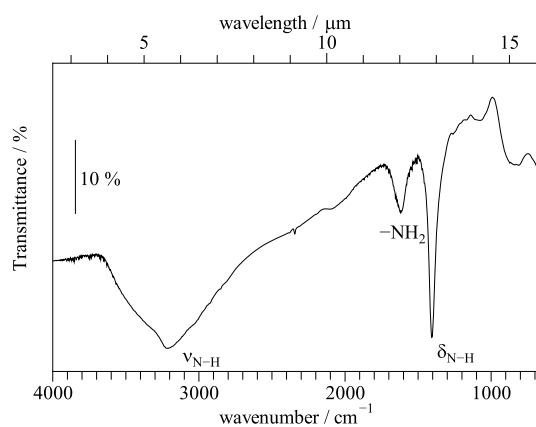
**3.1. Synthesis of  $\text{TiNCl}$  Using  $\text{NaNH}_2$ .** **3.1.1. Preliminary Reaction of  $\text{TiCl}_4$  with  $\text{NaNH}_2$ .** The sealed glass tube containing  $\text{TiCl}_4$  and  $\text{NaNH}_2$  was gradually heated up to

$150 \text{ }^\circ\text{C}$  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  $\text{TiCl}_4$  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  $\text{TiNCl}$ , but  $(\text{NH}_4)_2\text{TiCl}_6$  and low crystalline  $\text{TiN}$  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  $\text{TiCl}_4$  has reacted with  $\text{NH}_4\text{Cl}$  upon further heating  $\text{NH}_4\text{Cl}$ .  $\text{NH}_4\text{Cl}$  can be produced by the reaction of  $\text{TiCl}_4$  and  $\text{NH}_3$  emitted by the decomposition of  $\text{NaNH}_2$ .

On the other hand, the production of  $\text{TiN}$  suggests that a  $\text{Ti-NH}_2$  bond replaced at least one  $\text{Ti-Cl}$  bond in  $\text{TiCl}_4$ ; possibly, a titanium amide chloride such as  $\text{TiCl}_3(\text{NH}_2)$  is generated before the heating process. This  $\text{TiCl}_4$  ammonolysis reaction is energetically favorable.<sup>21,22</sup>  $\text{TiCl}_4$  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  $\text{TiCl}_4$  to finally form  $\text{TiCl}(\text{NH}_2)_3$ .<sup>13,23,24</sup>

**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  $\text{TiCl}_4$  with  $\text{NaNH}_2$ , as shown in Figure 1. Three prominent absorption bands were observed in the



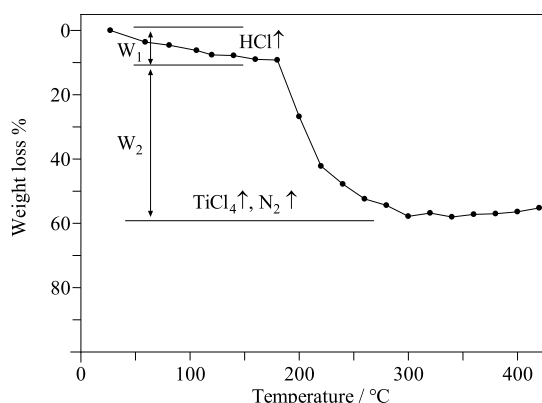
**Figure 1.** IR spectrum for the  $\text{TiCl}_4$  and  $\text{NaNH}_2$  mixture after heating at  $150 \text{ }^\circ\text{C}$ .

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

One more IR absorption band could be assigned to the  $-\text{NH}_2$  groups, which has been reported to appear at a frequency of  $1550 \text{ cm}^{-1}$ .<sup>26–28</sup> 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  $\text{TiCl}_4$ .<sup>26</sup> 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  $\text{TiNCl}$ .<sup>29</sup> Since  $\text{TiNCl}$  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  $\text{TiCl}_4$ ,  $\text{NaCl}$ ,  $\text{TiCl}_4 \cdot x\text{NH}_3$ , and a small amount of unreacted  $\text{NaNH}_2$ . 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.  $\text{NaNH}_2$  shows a slight  $\text{N}_2$  emission below 230 °C.<sup>30</sup> The weight reduction factor below 180 °C in this study is mainly attributed to the aminated  $\text{TiCl}_4$  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



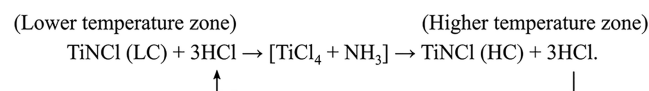
and so forth. However, the actual weight loss  $W_1$  was only 9.2%. This result indicates that the reaction had not completed at this temperature but would continue to a much higher temperature.

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:  $2\text{ZrCl}_3(\text{NH}_2) \rightarrow \text{ZrNCl} + \text{ZrCl}_4 + \text{NH}_4\text{Cl}$ .<sup>29</sup> On further heating up to 800 °C, the sample was decomposed to  $\text{ZrN}$ . In the present study, the decomposition temperature of  $\text{TiNCl}$  can be considerably lower than that of  $\text{ZrNCl}$ , especially if the unreacted  $\text{NaNH}_2$  exists as an even stronger reducing reagent. Then, the

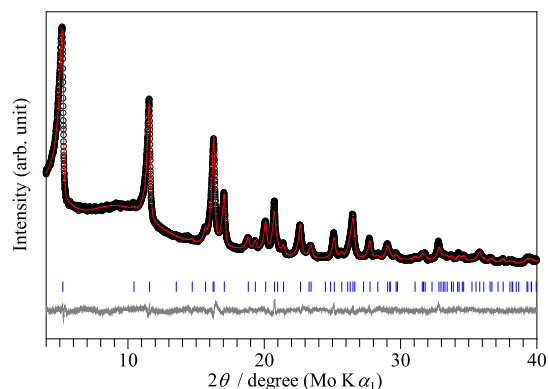
following reaction would have simultaneously occurred with reaction 1 above 200 °C;  $8\text{TiNCl} \rightarrow 2\text{TiCl}_4 + 6\text{TiN} + \text{N}_2$ . The weight loss for this reaction was calculated to be 52%. Although this value is in good agreement with the amount of the loss  $W_2$  (49%), 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  $\text{TiNCl}$ .** From these results, while the preliminary reacted solids include  $\text{Ti-NH}_2$  bonds, they contain unreacted  $\text{TiCl}_4$  and other ammonia complexes of  $\text{TiCl}_4$ . The procedures to obtain  $\text{TiNCl}$  using  $\text{NaNH}_2$  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  $\text{TiCl}_4$  is purged from the glass tube. Then, the preliminary reacted solids are evacuated again with an elevated temperature of 180 °C to remove  $\text{HCl}$  from  $\text{TiCl}_3(\text{NH}_2)$  and/or other aminated compounds. Here, we can obtain a low-crystallinity (LC)  $\text{TiNCl}$  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  $\text{TiN}$  occurs and sealed again into a glass tube. (4) The glass tube sends chemical transport to obtain highly crystalline (HC)  $\text{TiNCl}$ .

**3.1.6. Chemical Vapor Transport of  $\text{TiNCl}$ .** The following equation can simply describe the net chemical transport



$\text{HCl}$  is required to decompose LC  $\text{TiNCl}$  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- $\text{TiNCl}$ -containing materials as they are. A small amount of  $\text{NH}_4\text{Cl}$  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)  $\text{TiNCl}$  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



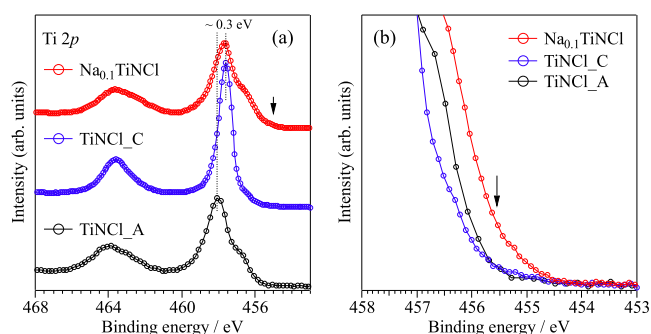
**Figure 3.** Rietveld analysis of the XRD pattern of  $\text{TiNCl}$  obtained in the process proposed in this study. Open circles show the observed data points, and the solid line represents the calculated diffraction pattern. The tick marks are the calculated  $2\theta$  angles for the Bragg peaks of  $\text{TiNCl}$ .

phase of TiNCl and agreed with the previously reported value.<sup>8</sup> 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.<sup>31</sup> 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.<sup>8</sup> 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 NaNH<sub>2</sub>.<sup>15</sup> 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.<sup>8</sup> The temperature dependence of resistance of TiNCl\_A is closer to hopping conduction,<sup>32</sup> 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  $\sim 1.5$  eV, comparable to the previously reported value (Figure S3).<sup>33</sup> 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*<sub>3/2</sub> and Ti 2*p*<sub>1/2</sub>, respectively, as shown in Figure 4a. The Ti 2*p*<sub>3/2</sub> peak has a broad shoulder-like component in the lower binding energy side, similar to the valence splitting of previously reported electron-doped samples.<sup>33,34</sup>



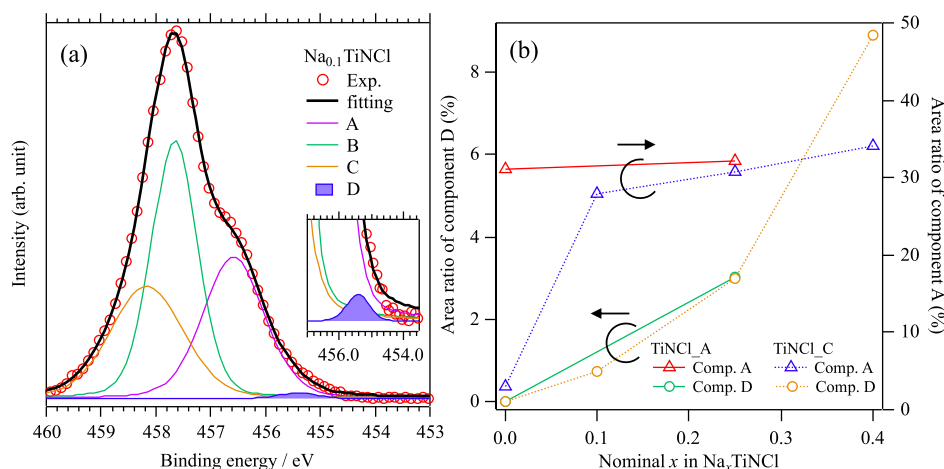
**Figure 4.** (a) Ti 2*p* core-level spectra of TiNCl obtained in this study (TiNCl\_A) compared with that obtained using the conventional method (TiNCl\_C) together with intercalated samples (Na<sub>0.1</sub>TiNCl). Each spectrum was normalized by the area of the peak. (b) Enlargement of the fine structure 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<sub>0.1</sub>TiNCl) when the peaks shifted 0.3 eV to the higher binding energy side. The intercalation compound Na<sub>0.1</sub>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<sub>0.1</sub>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<sub>0.1</sub>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<sub>0.1</sub>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 Ti<sup>3+</sup> content in the sample. Since the electron doping should increase the Ti<sup>3+</sup> 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 NaNH<sub>2</sub>. Some unreacted NaNH<sub>2</sub> remaining in the reaction cell may cause another reaction besides the proposed ideal reactions. The decomposition of NaNH<sub>2</sub> 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, NH<sub>3</sub>, H<sub>2</sub>, and N<sub>2</sub>, as the intermediate product.<sup>30</sup> There is another report that adding NaH to NaNH<sub>2</sub> suppresses the generation of ammonia and release H<sub>2</sub>.<sup>35</sup> The partial pressure of NH<sub>3</sub> is suppressed in the decomposition process, and the reaction may occur in the presence of H<sub>2</sub> or N<sub>2</sub> 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.<sup>31</sup> 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  $\text{TiNCl}_C$ . 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  $\text{TiNCl}_A$  and  $\text{TiNCl}_C$ .

sample morphology-dependent functionalities might also be expected in the present pristine  $\text{TiNCl}$ .

#### 4. CONCLUSIONS

We prepared a HC  $\text{TiNCl}$  using a reaction of  $\text{TiCl}_4$  with  $\text{NaNH}_2$  in a closed system. This report is the first example of synthesizing  $\text{TiNCl}$  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  $^{15}\text{N}$  isotope effect for elucidating the superconducting mechanism. It could be carried out not only for  $\text{TiNCl}$  but also for the other metal nitride superconductors. Furthermore, the obtained  $\text{TiNCl}$  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.<sup>8</sup>

#### ■ 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)

#### ■ AUTHOR INFORMATION

##### Corresponding Author

Masashi Tanaka – Graduate School of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan; [orcid.org/0000-0002-4323-5999](https://orcid.org/0000-0002-4323-5999); Phone: +81-93-884-3204; Email: [mtanaka@mns.kyutech.ac.jp](mailto:mtanaka@mns.kyutech.ac.jp)

##### Authors

Noriyuki Kataoka – Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan

Ryo Matsumoto – ICYS, National Institute for Materials Science, Tsukuba 305-0047, Japan; [orcid.org/0000-0001-6294-5403](https://orcid.org/0000-0001-6294-5403)

Kei Inumaru – Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan; [orcid.org/0000-0001-6876-3854](https://orcid.org/0000-0001-6876-3854)

Yoshihiko Takano – MANA, National Institute for Materials Science, Tsukuba 305-0047, Japan; Research Institute for Interdisciplinary Science (RIIS), Okayama University, Okayama 700-8530, Japan

Takayoshi Yokoya – Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan; [orcid.org/0000-0002-1251-2826](https://orcid.org/0000-0002-1251-2826)

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.1c06986>

#### Author Contributions

#M.T. and N.K. contributed equally.

#### Notes

The authors declare no competing financial interest.

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