Synthesis and Electron Doping of TiNCl

Layered metal nitride halides MNX (M = Ti, Zr, Hf; X = Cl, Br, I) have two polymorphs, including α- and β-forms, which have the FeOCl and SmSI structures, respectively. These compounds are band insulators and become metals and show superconductivity after electron doping by intercalating alkali metals between the layers. The superconductivity of β-form had been extensively characterized from decades ago, but it is not easy to consistently interpret all experimental results using conventional phonon-mediated Bardeen–Cooper–Schriefer mechanisms. The titanium compound TiNCl crystallizes only in the α-form structure. TiNCl also exhibits superconductivity as high as ~16 K after electron doping by intercalating metals and/or organic basis. It is important to compare the superconductivity of different M–N networks. However, α-form compounds are vulnerable to moisture, unlike β-form ones. The intercalation compounds are even more sensitive to humid air.

## 1. Introduction

Transition metal nitride halides MNX (M = Ti, Zr, Hf; X = Cl, Br, I) belong to a characteristic class of layered materials that exhibits superconductivity by carrier doping [1][2][3]. They have two polymorphs, including α- and β-forms, which have the FeOCl and SmSI structures, respectively [4][5]. These compounds are band insulators and can be intercalated with alkali or alkaline earth metals to significantly modify the physical properties without changing their basic crystal structures. Alkali atoms with/without organic molecules are intercalated into the van der Waals gap between two adjacent X layers with the realignment of MNX layers.

The β-form polymorph contains double honeycomb-like MN layers sandwiched by halogen layers. Band-insulating β-HfNCl is electron-doped and becomes metallic through intercalation [2][4]. The compound shows superconductivity at a transition temperature (T_c) above 25.5 K in Li and tetrahydrofuran (THF) cointercalated compound of β-HfNCl [2][4][6]; this family of materials is categorized as high-T_c superconductors. The superconductivity can also be induced by carrier doping with an electronic-double-layer transistor [7][8][9][10][11]. The T_c enhancement has been reported with reducing carrier density [12][13] and the partial substitution M site [14]. Electronic structural studies have shown that alkali-metal intercalation adds quasi-two-dimensional electronic states near the Fermi level (E_F), which are hybridized states of Hf 5d and N 2p orbitals [15][16][17][18][19]. The absence of isotope effect, extremely large superconducting gap value $2\Delta/k_B T_c$, enhancement of T_c for lower carrier concentration, anomalous doping dependence in anisotropy of superconducting gap, and strong suppression of the coherence peak in nuclear spin-lattice relaxation rate strongly suggest an exotic superconducting state in this material series [13][20][21][22][23][24][25][26][27][28]. With the extensively characterized superconductivity in β-form MNX, it is not easy to consistently interpret all experimental results using conventional phonon-mediated Bardeen–Cooper–Schrieffer (BCS) mechanisms [29].

2. Conventional Preparation

For the synthesis of MNX, the tetrahalides of titanium, zirconium, and hafnium are reacted with ammonia following the generic equation:

$$MX_4 + 4NH_3 \rightarrow MNX + 3NH_4X$$
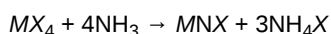
In the case of M = Zr, Hf in the β-form, Yamanaka has efficiently developed the method using a reaction of metal or metal hydride powders with NH_4X [3]. The one-step method in a vacuum-sealed glass tube can also be adopted in a small-scale synthesis of less than ~200 mg [2].

However, in the case of M = Ti, especially TiNCl, the easy process cannot be used. In the reaction between Ti and NH_4Cl, TiH_2 is first formed at about 400 °C or lower. Above the temperature at which TiH_2 can be decomposed, TiNCl is not

formed, but TiN is formed instead. Then, the ammonia (NH_3) gas should be passed over titanium tetrachloride ($TiCl_4$) in a vertical Pyrex glass reaction cell. The reactant becomes black solid after being self-heated by the heat evolved from the intense exothermic reaction. Due to the high reactivity of $TiCl_4$ with NH_3, the reaction may lead to molecules and complexes of several manners [30]. $TiCl_4$ ammonolysis is energetically favorable [30][31]. $TiCl_4$ forms ammonia-incorporated complexes with the $TiCl_4 \cdot xNH_3$ gross composition, and heating the complexes in ammonia-rich atmosphere results in stepwise amination of $TiCl_4$ to form $TiCl(NH_2)_3$ in the final step [32][33][34]. The ammonia complexes and aminated $TiCl_4$ were especially the main products at low temperatures below 400 °C [32], while TiN is obtained at higher temperatures. The resulting solids were continuously heated in the same reaction cell at 400 °C for 3–5 h under the ammonia gas stream. Ammonium chloride (NH_4Cl) crystals were grown on the upper part of the reaction cell.

The TiNCl precursor and other related compounds (crude mixture) were formed at the bottom of the glass cell. The by-products necessitate a next purification step. The crude mixture was vacuum-sealed in a Pyrex glass tube with a small amount of NH_4Cl and put into a horizontal furnace with a temperature gradient for one to two weeks. Then, it was purified into highly crystalline TiNCl by chemical transport using NH_4Cl. The end of the glass tube containing the mixture was maintained at 380 °C in the lower temperature zone, and the other end of the glass tube was placed in the higher temperature zone. Purified TiNCl was obtained at the higher temperature zone [35]. TiNCl starts to decompose to TiN at temperatures above 400 °C [36][37]. Once it decomposes into TiN with trivalent titanium, it is hard to return to tetravalent TiNCl. Then, it should be maintained at a temperature as low as possible above 400 °C to obtain impurity-free samples.

Assuming the same reaction as the case of ZrNCl [38], the essential reaction in the chemical vapor transport of TiNCl is expressed as follows:

$$TiCl_4(g) + NH_3(g) \rightarrow TiCl_3(NH_2) + HCl \rightarrow TiNCl(s) + 3HCl(g) (>{\sim}400 °C)$$

Since HCl is not easy to handle in this preparation, it is used as a transport agent by utilizing the dissociation of NH_4Cl into NH_3 and HCl at high temperatures. The actual reaction is then expressed as

$$TiCl_3(NH_2) + NH_4Cl \rightarrow TiNCl(s) + NH_3(g) + HCl(g)$$

After these reactions, it can be confirmed the purity of the obtained TiNCl by the Rietveld refinement and magnetization measurement with the negligible diamagnetic contribution of TiN below 5 K.

3. Preparation Using Sodium Amide

In a study on a superconducting mechanism, the isotope effect on T_c provides crucial evidence of whether electron–phonon interaction is responsible for superconductivity. Considering the above conventional synthesizing process of TiNCl, retaining the ^{15}N isotope using NH_3 gas as a nitrogen source is extremely difficult or almost impossible realistically. However, if the TiNCl precursor could be formed using a solid reagent other than gas NH_3 as a nitrogen source in a closed reaction cell, an essential technique for synthesizing ^{15}N substituents would be developed. It could be led not only to elucidate the superconducting mechanism of TiNCl but also to investigate the isotope effect of other metal nitride superconductors.

$NaNH_2$ is a highly reactive solid nitrogen source used for combustion reaction with $3d$ transition metal chlorides to obtain metal nitrides [39][40]. The reactions are thermodynamically driven by a metathesis reaction involving the formation of stable NaCl. The NaCl does not contribute to chemical transport; if the reaction with $TiCl_4$ can be controlled, TiNCl may be obtained in the sealed glass tube.

When the sealed glass tube containing $TiCl_4$ and $NaNH_2$ was gradually heated up to 150 °C in 12 h and then kept at this temperature for 1-2 days, the infrared spectroscopy, thermogravimetry, and X-ray diffraction measurements of the resulting solids suggested that it contains $TiCl_3(NH_2)$, $TiCl_2(NH_2)_2$, and $TiCl(NH_2)$, together with $TiCl_4 \cdot xNH_3$ [41]. Namely, the reaction at this process can be written as the equation $TiCl_4 + NaNH_2 \rightarrow TiCl_3(NH_2) + NaCl$ in the simplest case. After an important process of removing HCl from the reaction system, researchers can obtain TiNCl with the whole equation in the simplest case written in $TiCl_4 + NaNH_2 \rightarrow TiCl_3(NH_2) + NaCl \rightarrow TiNCl + NaCl + 2HCl$.

The procedures to obtain TiNCl using $NaNH_2$ can be summarized as the following. (1) The sealed mixture of $TiCl_4$ + $NaNH_2$ is sufficiently reacted around 160 °C to obtain preliminary reacted solids. (2) Open the seal and purge unreacted $TiCl_4$ from the glass tube. Then, evacuate the preliminary reacted solids again with the elevated temperature at 180 °C to remove HCl from $TiCl_3(NH_2)$ and/or other aminated compounds. (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 to chemical transport to obtain highly crystalline TiNCl [41].

4. Electron Doping by Intercalation

Metal intercalation into TiNCl was developed from an electrochemical process as a cathode material [42]. First, superconducting TiNCl has been achieved by an organic Lewis base pyridine (Py) and alkali metal intercalation [3]. The alkali-metal-intercalated TiNCl was prepared using reactions with alkali metal azides at elevated temperatures of 280–350 °C in a vacuum. The intercalation was carried out in the following manner:

$$TiNCl + (x + y)\,A N_3 > A_y TiNCl_{1-x} + xACl + 3(x + y)/2 N_2$$

This reaction was not mild, and partial deintercalation of chlorine atoms occurred simultaneously. The superconducting volume fractions (VF) were as low as 0.1–30%. The samples may have suffered from serious structural damage.

A chemical intercalation method using alkali-metal naphthalene solutions in THF (A-Naph/THF; A = Li, Na, K, Rb) has been used for β-phase for a long time [43]. This method has dramatically improved the low VF problem [44]. Organic molecules such as THF can be cointercalated into TiNCl at room temperature. The THF-cointercalated phase was changed into the uncointercalated compound A_xTiNCl by evacuation. The sample thus obtained showed a shielding VF close to 100% and a clear high onset superconducting transition. By this method, the same α-phase TiNBr has also succeeded in being a superconductor [45]. On the other hand, α-HfNBr isomorphous with TiNCl did not show superconductivity in the same method. The resistivity was larger than ~10^7 Ω cm; the doped electrons seem to be localized on the reduced Hf sites [46]. It should be noted that only Py intercalated TiNCl showed superconductivity. It appears the combination of guest donors and the amount of doping are important to realize the superconductivity of the α-form MNX.

The T_c changes with the basal spacing d along the c axis of the intercalation compound. The T_c decreases with the increasing d [44]. This fact is in sharp contrast to the observation in β-form, where T_c increases linearly with d in electron-doped ZrNCl and HfNCl [25][47]. The data fit on a linear line with passing through the origin. This fact suggests that the Coulomb interlayer coupling in the pairing mechanism is important in this system [44]. Another study on the α-TiNBr has demonstrated a similar linear relation on the T_c vs. $1/d$ [45]. Harshman et al. reported that the linear dependence is readily explained, giving the interlayer Coulomb interaction model and structure [48]. It is also a future task to experimentally observe the effect of the interlayer interaction on the electronic structure.

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