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# Ammonolysis of $HTiNbO_5$–*n*-Propylamine Intercalation Compound

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The ammonolysis reaction to form (Ti,Nb)N was enhanced by the use of $HTiNbO_5$–*n*-propylamine intercalation compound as a starting material and compared with that for a simple mixture of $TiO_2$ and $Nb_2O_5$. The ammonolysis product formed at 1200 °C was a superconductor ($T_c = 15\,K$) with a rock-salt crystal structure having many structural defects along the stacking direction of the intercalation compound.

Oxynitrides have attracted interest for application as white light-emitting diode (LED) phosphors,[1,2] possible lead-free dielectric materials,[3,4] new superconductors,[5,6] inorganic pigments,[7,8] and as photocatalysts.[9–11] Oxynitrides that contain more than two different cations are of significant interest for improvement of these properties. Such compounds have been prepared by the ammonolysis of metal oxide mixtures; however, the variation of compounds is still very limited, partly due to the poor kinetics for the ammonolysis reaction. Ammonolysis of amorphous oxide mixtures prepared through a citrate route improved access to new oxynitrides such as $RE_2Ta_2O_5N_2$ pyrochlores (RE = Nd–Gd), $RETa(O,N,\square)_4$ disordered fluorites (RE = Dy–Yb),[12,13] wurtzite-type gallium oxynitride compounds doped with various transition-metal cations,[14–19] and europium-doped aluminum oxynitride.[20,21] Double metal oxides, especially nanopowders of such, would also contribute to enhance the ammonolysis reaction to obtain new oxynitrides.

$KTiNbO_5$ is a layered compound with interleaved potassium ions between $(TiNbO_5)^-$ oxide layers.[22] It can intercalate *n*-propylamine after potassium ion exchange with protons during treatment of $KTiNbO_5$ with HCl.[23] The interlayer distance expands more than twice during the intercalation process to exfoliate the oxide layers, which results in an exfoliated nanopowder that would be highly reactive for ammonolysis.

In the present study, ammonolysis behavior was studied for the $HTiNbO_5$–*n*-propylamine intercalation compound and compared with the nitridation reaction of a mixture of $TiO_2$ and $Nb_2O_5$ (2:1 molar ratio). The crystal structure and superconductivity behavior of the nitrided products were also investigated.

$KTiNbO_5$ was prepared by firing a mixture of $K_2CO_3$, $TiO_2$, and $Nb_2O_5$ in a molar ratio of 1.1:2:1 at 1100 °C for 20 h. The product (ca. 1 g) was reacted at 35 °C for 1 day with 120 mL of *n*-propylamine after treatment with HCl to form $HTiNbO_5$, as described in our previous report.[23] The *n*-propylamine-intercalated $HTiNbO_5$ was nitrided in the temperature range between 500 and 1200 °C for 15 h in an ammonia flow of $50\,mL\,min^{-1}$. A mixture of $TiO_2$ and $Nb_2O_5$ with an average grain size of 200 and 300 nm, respectively, in a molar ratio of 2:1 was also nitrided under the same firing conditions as a reference.

Orthorhombic lattice parameters changed from $a = 0.6439$, $b = 0.3796$, $c = 1.838\,nm$ for $KTiNbO_5$ to $a = 0.6534$, $b = 0.3776$, $c = 1.661\,nm$ for $HTiNbO_5$ and then to $a = 0.6428$, $b = 0.3813$, $c = 3.486\,nm$ for the intercalated $HTiNbO_5$–*n*-propylamine. The *c* parameter was approximately doubled along the layer stacking direction by *n*-propylamine intercalation.[23] Cleavage of the platy crystals was clearly observed along the plane after *n*-propylamine intercalation, as shown in Figure 1. X-ray fluorescence analysis indicated the molar ratio of Ti:Nb had been kept at 1:1 after the intercalation reaction.

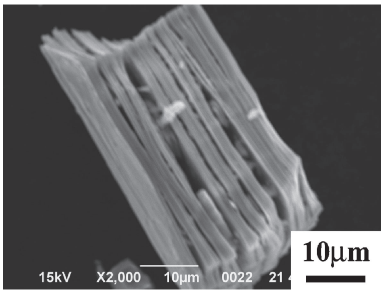

**Figure 1.** SEM photograph of an *n*-propylamine-intercalated $HTiNbO_5$ crystal.

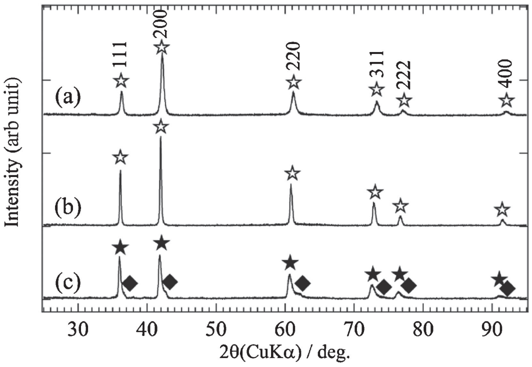

**Figure 2.** Powder X-ray diffraction patterns for the ammonolysis products from (a) $HTiNbO_5$–*n*-propylamine at 800 °C, (b) $HTiNbO_5$–*n*-propylamine at 1000 °C, and (c) a mixture of $TiO_2/Nb_2O_5 = 2/1$ in molar ratio at 1000 °C. Diffraction lines marked with open, filled stars, and filled diamonds were assigned to those of $(Ti_{0.5}Nb_{0.5})N$, $(Ti_{1-x}Nb_x)N$ with $x > 0.5$ and $x < 0.5$, respectively.

Ammonolysis at 800 °C converted $HTiNbO_5$–*n*-propylamine to $(Ti_{0.5}Nb_{0.5})N$, as depicted in Figure 2. The crystallinity of the nitrided product was improved by ammonolysis at 1000 °C. The cubic lattice parameter increased from $a = 0.4283\,nm$ at 800 °C to 0.4302 nm at 1200 °C, which was slightly smaller than the reported value of 0.4328 nm.[24] The nitrided product had small amounts of oxygen impurity and cation vacancy in its rock salt lattice as mentioned below. The nitrided product prepared from a mixture of $TiO_2$ and $Nb_2O_5$ under the same conditions was a mixture of isostructural $(Ti_{1-x}Nb_x)N$ compounds having two compositions, $x > 0.5$ and $x < 0.5$, due to inhomogeneous reaction. The nitrided products of the intercalation compound at 1200 °C exhibited superconductivity below $T_c = 15\,K$ and the volume fraction was 85%. The values of $T_c$ and the volume

**Table 1.** Superconductive characteristics, nitrogen and oxygen content of the nitrided HTiNbO$_5$–*n*-propylamine at various temperatures

| Ammonolysis temperature /°C | $T_c$ /K | Volume fraction /% | Molar ratio | |
|---|---|---|---|---|
| | | | N/(O + N) | (Ti + Nb)/(O + N) |
| 1200 | 15 | 85 | 0.99 | 0.93 |
| 1000 | 15 | 80 | 0.96 | 0.88 |
| 900 | 12 | 55 | 0.91 | 0.86 |
| 800 | 7 | 20 | 0.85 | 1.15 |

fraction decreased with the decreasing ammonolysis temperature, as summarized in Table 1. The temperature was lower than the reported value of 17.5 K,[25] probably due to the structural imperfection originated from the intercalated layer structure as described in next section. The oxygen and nitrogen contents were measured with an oxygen/nitrogen analyzer (EMGA-620W, Horiba) using inert gas fusion method. The observed molar ratios of N/(O + N) and (Ti + Nb)/(O + N) are shown in Table 1. The nitrogen molar ratio was increased in the total amount of anions with the increasing ammonolysis temperature; however a small amount of cation vacancy of 7% was still present in the rock-salt lattice nitrided at 1200 °C.

The relative intensity of the X-ray diffraction pattern for the 1000 °C nitrided product ($Ti_{0.5}Nb_{0.5}$)N was not well simulated with the rock-salt-type crystal structure by refining the 4*a* site cation occupancy of Ti and Nb in $Fm\bar{3}m$ with some amount of vacancies. The relative diffraction intensity should not be affected by the preferred orientation in an isotropic crystal structure such as $Fm\bar{3}m$ but by some type of disordering such as an imperfection of long range ordering along the direction in the previous $(TiNbO_5)^-$ layer stacking. The radial distribution around Nb was obtained by Fourier transform of the Nb K-edge extended X-ray absorption fine structure (EXAFS). The first nearest neighbors for Nb–(N,O) appear at 0.17 nm for the present nitrided products, as well as for the commercially available NbN, as depicted in Figure 3. The second nearest neighbor for Nb–Nb was observed at 0.27 nm in NbN, and its intensity was stronger than that for the first nearest Nb–N, due to the much larger X-ray scattering factor in Nb than in N, which was very weak for the present nitrided products. The rock-salt-type crystal lattice was much more easily formed within than across the $(TiNbO_5)^-$ layers in the intercalated compound, because of the much shorter contact distance between $TiO_2$ and $Nb_2O_5$ within the layers. The stacking defects lead to the psuedo two dimensional rock-salt-type lattice and reduced the radial distribution intensity for the second nearest neighboring Nb–(Nb,Ti).

In conclusion, superconducting ($Ti_{0.5}Nb_{0.5}$)N was prepared by the ammonolysis of the HTiNbO$_5$–*n*-propylamine intercalation compound at a relatively lower temperature than that for preparation from a mixture of $TiO_2$ and $Nb_2O_5$. The crystal structure was assumed to be a rock-salt-type with a large stacking disorder along the stacking direction in the layer structure of the HTiNbO$_5$ starting material.

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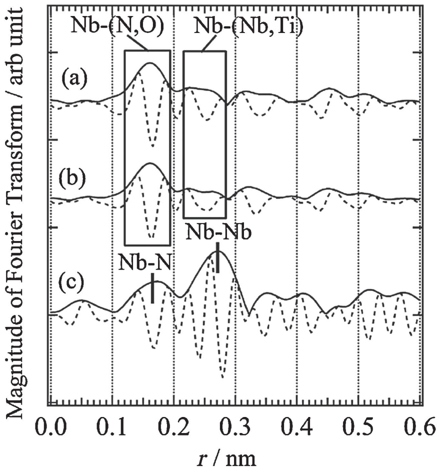

**Figure 3.** Fourier transformation of EXAFS in X-ray absorption spectra; (a) nitrided HTiNbO$_5$–*n*-propylamine at 1000 °C, (b) nitrided HTiNbO$_5$–*n*-propylamine at 800 °C and (c) NbN reference, respectively.

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