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## Ammonolysis of HTiNbO<sub>5</sub> (n-propyl amine) Intercalation Compound

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The ammonolysis reaction to form (Ti,Nb)N was enhanced by the use of the HTiNbO<sub>5</sub> (n-propyl amine) intercalation compound as a starting material compared with that for a simple mixture of TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>. The ammonolysis product formed at 1200 °C was a superconductor (T<sub>c</sub> = 15 K) with a rock-salt type 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,<sup>1,2</sup> possible lead-free dielectric materials,<sup>3,4</sup> new superconductors,<sup>5,6</sup> inorganic pigments,<sup>7,8</sup> and as photocatalysts.<sup>9-11</sup> 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 the problem to develop new oxynitrides such as RE<sub>2</sub>Ta<sub>2</sub>O<sub>5</sub>N<sub>2</sub> pyrochlores (RE = Nd~Gd), RETa(O,N,□)<sub>4</sub> disordered fluorites (RE = Dy~Yb)<sup>12,13</sup>, wurtzite-type gallium oxynitride compounds doped with various transition metal cations<sup>14-19</sup>, and europium doped aluminum oxynitride.<sup>20,21</sup> Double metal oxides, especially nanopowders of such, would also contribute to enhance the ammonolysis reaction to obtain new oxynitrides.

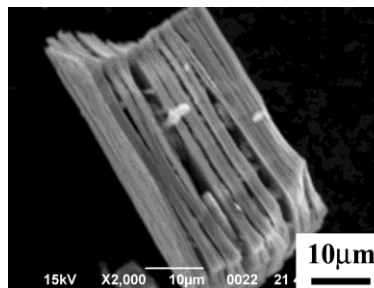
KTiNbO<sub>5</sub> is a layered compound with interleaved potassium ions between (TiNbO<sub>5</sub>)<sup>-</sup> oxide layers.<sup>22</sup> It can intercalate n-propyl amine after potassium ion exchange with protons during treatment of KTiNbO<sub>5</sub> with HCl.<sup>23</sup> The interlayer distance 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<sub>5</sub> (n-propyl amine) intercalation compound and compared with the nitridation reaction of a mixture of TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> (2:1 molar ratio). The crystal structure and superconductivity behavior of the nitrided products were also investigated.

KTiNbO<sub>5</sub> was prepared by firing a mixture of K<sub>2</sub>CO<sub>3</sub>, TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> 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-propyl amine after treatment with HCl to form HTiNbO<sub>5</sub>, as described in our previous report.<sup>23</sup> The n-propyl amine intercalated HTiNbO<sub>5</sub> was nitrided in the temperature range between 500 and 1200 °C for 15 h in an ammonia flow of 50 mL/min. A mixture of TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> with an average grain size of 200 nm and 300 nm, respectively, in a molar ratio of

2:1 was also nitrided under the same firing conditions as a reference.

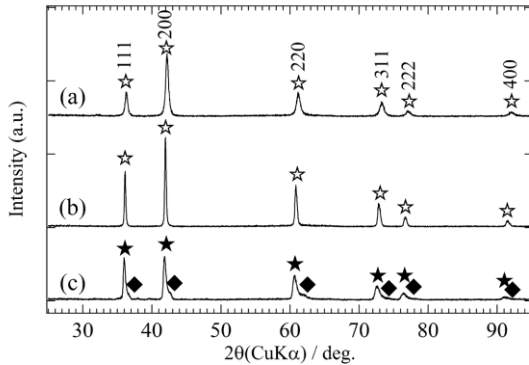
Orthorhombic lattice parameters changed from a = 0.6439, b = 0.3796, c = 1.838 nm for KTiNbO<sub>5</sub> to a = 0.6534, b = 0.3776, c = 1.661 nm for HTiNbO<sub>5</sub> and then to a = 0.6428, b = 0.3813, c = 3.486 nm for the intercalated HTiNbO<sub>5</sub> (n-propyl amine). The c-parameter was approximately doubled along the layer stacking direction by n-propyl amine intercalation.<sup>23</sup> Cleavage of the platy crystals was clearly observed along the plane after n-propyl amine intercalation, as shown in Fig. 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-propyl amine intercalated HTiNbO<sub>5</sub> crystal.

Ammonolysis at 800 °C converted HTiNbO<sub>5</sub> (n-propyl amine) to (Ti<sub>0.5</sub>Nb<sub>0.5</sub>)N, as depicted in Fig. 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.<sup>24</sup> 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<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> under the same conditions was a mixture of isostructural (Ti<sub>1-x</sub>Nb<sub>x</sub>)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<sub>c</sub> = 15 K and the volume fraction was 85%. The values of T<sub>c</sub> and the volume fraction decreased with the decreasing ammonolysis temperature, as summarized in Table 1. The temperature was lower than the reported value of 17.5K,<sup>25</sup> 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 nitrated at 1200 °C.

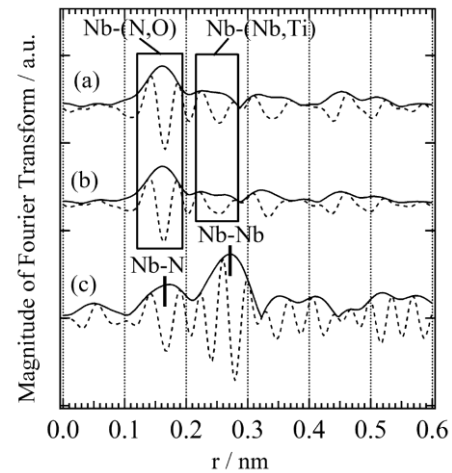


**Figure 2.** Powder X-ray diffraction patterns for the ammonolysis products from (a) HTiNbO<sub>5</sub> (n-propyl amine) at 800°C, (b) HTiNbO<sub>5</sub> (n-propyl amine) at 1000°C and (c) a mixture of TiO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub> = 2/1 in molar ratio at 1000°C. Diffraction lines marked with open, filled stars, and crosses were assigned to those of (Ti<sub>0.5</sub>Nb<sub>0.5</sub>)N, (Ti<sub>1-x</sub>Nb<sub>x</sub>)N with  $x > 0.5$  and  $x < 0.5$ , respectively.

**Table 1.** Superconductive characteristics, nitrogen and oxygen content of the nitrated HTiNbO<sub>5</sub> (n-propyl amine) at various temperatures.

Ammonolysis temperature/°C	T <sub>c</sub> /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

The relative intensity of the X-ray diffraction pattern for the 1000 °C nitrated product (Ti<sub>0.5</sub>Nb<sub>0.5</sub>)N was not well simulated with the rock-salt type crystal structure by refining the 4a site cation occupancy of Ti and Nb in *Fm-3m* 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-3m*, but by some type of disordering such as an imperfection of long range ordering along the direction in the previous (TiNbO<sub>5</sub>)<sup>-</sup> 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 nitrated products, as well as for the commercially-available NbN, as depicted in Fig. 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 nitrated products. The rock-salt type crystal lattice was much easily formed within than across the (TiNbO<sub>5</sub>)<sup>-</sup> layers in the intercalated compound, because of the much shorter contact distance between TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> within the layers. The stacking defects lead to the pseudo two dimensional rock-salt type lattice and reduced the radial distribution intensity for the second nearest neighboring Nb-(Nb,Ti).



**Figure 3.** Fourier transformation of EXAFS in X-ray absorption spectra; (a) nitrated HTiNbO<sub>5</sub> (n-propyl amine) at 1000 °C, (b) nitrated HTiNbO<sub>5</sub> (n-propyl amine) at 800 °C and (c) NbN reference, respectively.

In conclusion, superconducting (Ti<sub>0.5</sub>Nb<sub>0.5</sub>)N was prepared by the ammonolysis of the HTiNbO<sub>5</sub> (n-propyl amine) intercalation compound at a relatively lower temperature than that for preparation from a mixture of TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>. 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<sub>5</sub> starting material.

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**NOTE** The diagram is acceptable in a colored form. Publication of the colored G.A. is free of charge. For publication, electronic data of the colored G.A. should be submitted. Preferred data format is EPS, PS, CDX, PPT, and TIFF. If the data of your G.A. is "bit-mapped image" data (not "vector data"), note that its print-resolution should be 300 dpi.

