Synthesis and Crystal Structure of a New Niobium Oxynitride, $Nb_2N_{0.88}O_{0.12}$

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A new niobium oxynitride $Nb_2N_{0.88}O_{0.12}$ has been synthesized by reducing Nb_2O_5 in a stream of H_2 gas containing 0.07% N_2 at 1080°C for 5 weeks. The compound crystallizes in a hexagonal system with space group $P\bar{3}1m$, and $Z = 3$. The lattice parameters are $a = 5.2916 \pm 0.0001$ Å and $c = 4.9987 \pm 0.0001$ Å. In this space group, the nitrogen/oxygen atoms statistically occupy the $1a$ and $2d$ positions, and niobium atoms occupy the $6k$ position. This structure is the same as that of β-Nb_2N (ε-Fe_2N type), and the compound is regarded as a solid solution of β-Nb_2N and hypothetical Nb_2O of the same crystal structure. The crystallographic parameters were refined by using the Rietveld method. The chemical bonding of this compound seems to have a significant covalent and/or metallic character in the ionic bonding. © 2000 Academic Press

Key Words: niobium oxynitride; H_2 reduction; crystal structure; Rietveld refinement.

INTRODUCTION

High-temperature reduction of Nb_2O_5 with H_2 yields a variety of niobium oxides with different crystal structures (1). The bluish-black dioxide NbO_2 obtained by the reduction has a distorted rutile structure. Between Nb_2O_5 and NbO_2 there is a homologous series of structurally related phases of general formula $Nb_{3n+1}O_{8n-2}$ with $n = 5, 6, 7$, and 8. These phases can be explained by the shear structures with deficient O atoms formed from Nb_2O_5. Further reduction produces gray monoxide NbO, which is cubic and shows metallic conductivity (1). This structure is a unique variant of the NaCl structure in which there are vacancies of Nb at the eight corners of the unit cell and an O vacancy at its center. In the crystal the Nb and O atoms from four coplanar bonds. A characteristic feature of this structure is a 3D framework of Nb_6 octahedral clusters, which could be associated with the metallic conductivity of NbO. Reduction of NbO over long periods results in formation of niobium suboxides $NbO_{0.9}$ (2), $NbO_{0.73}$ (2), and Nb_2O

(2, 3). However, little is known about the effect of N_2 coexisting in H_2 gas on these suboxides.

Niobium oxynitrides have been synthesized by ammonolysis of niobium oxides, in which ammonia behaves simultaneously as reducing and nitriding agent. Schönberg obtained a face-centered cubic niobium oxynitride $NbN_{0.9}O_{0.1}$ by the ammonolysis of niobium oxides or ammonium niobates (4). Brauer synthesized the following two oxynitrides by ammonolysis of niobium pentoxide at 750°C (5). One is δ-Nb(O, N) ($Nb_{0.69}N_{0.75}O_{0.25}$), having a metal-deficient rock-salt lattice similar to δ-NbN with random distribution of N and O atoms over the entirely filled nonmetal positions and with only partly occupied metal positions. The other is ε-Nb(O, N) ($Nb_{0.82}N_{0.81}O_{0.19}$) having a hexagonal lattice similar to ε-NbN. These compounds were unstable above 900°C and decompose into niobium oxide NbO_2 and nitrides δ-NbN and/or β-Nb_2N. Recently, niobium oxynitrides have attracted attention to catalytic activities for hydrodesulfurization and hydrodenitrogenation of hydrocarbons. Optimization of the nitridation process by ammonolysis was investigated in order to obtain high specific surface area (6, 7). On the other hand, Roy *et al.* investigated the preparation of fcc type niobium oxynitrides in the form of thin films, by the reactive RF-sputtering technique (8). The films showed a higher superconducting transition temperature T_c compared to corresponding niobium nitride films. Houmes and zur Loye prepared the niobium oxynitrides $Nb_5N_{6-\delta}O_y$ of a hexagonal structure by reacting iron-containing precursors with flowing ammonia at 700 and 900°C (9). Some bimetallic oxynitrides containing niobium were also synthesized by nitriding bimetallic oxide precursors with ammonia gas (10, 11).

In the present work, reduction of Nb_2O_5 with H_2 gas containing a slight amount of N_2 was studied at a higher temperature, 1080°C. A new niobium oxynitride of much smaller (N, O)/Nb ratio, i.e., $Nb_2O_{0.88}O_{0.12}$, was obtained in a single phase. Its crystal structure was determined by powder X-ray diffractometry.

EXPERIMENTAL

Sample Preparation

The starting material, Nb_2O_5 of analytical grade ($H-Nb_2O_5$ phase; particle size, 0.15 µm), was purchased from Wako Pure Chemicals Ind., Ltd. The Nb_2O_5 powder was finely ground in an agate mortar and then pelletized into a disk of 10-mm diameter and ca. 2-mm thickness by using a uniaxial press at 10 MPa. The Nb_2O_5 pellets on an alumina boat were placed in an alumina tube of a horizontal Siliconit tube furnace. The reaction system was carefully checked for leakage of vacuum before and after the reaction. After evacuating the system, H_2 gas was introduced. The N_2 content in the H_2 gas was found to be 0.07% by gas chromatography using CHROMPACK, MicroGC CP2002. On the other hand, the O_2 was not detected by the same method, indicating that the partial pressure of oxygen was less than the detection limit. With a flow of the H_2 gas at a rate of 100 ml/min, the furnace temperature was subsequently raised to 1200°C in 10 h. At this temperature Nb_2O_5 was heated for 2 weeks. A gas bubbler containing silicone oil was used at the gas outlet for preventing air-backflow. After the product was cooled to room temperature, it was quickly taken out and put into a glass vessel, which was then evacuated to avoid oxidation. Some of the product pellets were crushed and ground for X-ray diffraction measurement. Thereafter, the sample was again heated at 1150°C for 2 weeks and then at 1100°C for 2 weeks. As another heating program, and Nb_2O_5 starting material was heated at 1080°C for 3 weeks. After XRD measurement, the sample was again heated at the same temperature of 1080°C for 2 more weeks. To calculate the composition of the products, the nitrogen content was determined by the traditional Kjeldahl methods, and the niobium content was obtained gravimetrically by oxidizing the compound to Nb_2O_5 in air at 800°C. The oxygen content was calculated by weight difference.

X-Ray Diffraction Analysis

X-ray powder diffractometry was carried out with a Rigaku Type RAD-IC diffractometer using CuKα radiation (40 kV, 20 mA) monochromatized with curved pyrolytic graphite. The slit system used was 1°–0.5 mm–1°–0.15 mm. The measurement was made in the range $10° \leqq 2\theta \leqq 130°$ with a scanning rate of 1°/min (Bragg–Brentano geometry). The diffraction data were recorded in steps of 0.02° in 2θ. Calculation of the possible crystal system and space group was performed with the aid of the CELL program (12) using about 24 measured peaks. The lattice parameters and the theoretical values of peak positions and intensities were calculated by the LCR2 (13) and LAZY-PULVERIX (14) programs, respectively. The program RIETAN (15) was used for refining the crystal

structures by the Rietveld method. The fitting procedure was conducted using the intensity data of 24 peaks in the range of $10° \leqq 2\theta \leqq 130°$.

Density Measurement

The density of the product was determined by the toluene displacement method. About 1.5 g of the sample powder was precisely weighed in a glass bulb (7.423 g in weight with 2.863 ml inner volume) first in air then in toluene at 22°C. To minimize the systematic error from open pores in the powder sample, the bulb containing the sample and toluene was put in a desiccator and evacuated until bubble formation from the open pores ceased.

Determination of Niobium Valence

The valence of niobium in $Nb_2N_{0.88}O_{0.12}$ was determined by the cerium back-titration method. About 10 mg $Nb_2N_{0.88}O_{0.12}$ powder was weighed to an accuracy of ± 10 µg and dissolved in a 5-ml Ce(IV) solution of 1.5 M sulfuric acid. Assuming that the Ce(IV) was used only for the oxidation of niobium, the valence of niobium was obtained by titrating the excess Ce(IV) with standard Fe(II) ammonium sulfate solution using a ferroin indicator.

RESULTS AND DISCUSSION

Preparation of $Nb_2N_{0.88}O_{0.12}$

The X-ray diffraction patterns of samples heated at 1100, 1150, and 1200°C are given in Fig. 1. These results were obtained by changing both the temperature and the reaction time. The pattern for the 1200°C sample consists of a mixture of two phases. At this reaction temperature, a large amount of cubic NbO, the peaks of which are shown in the figure as squares, coexists with $Nb_2N_{0.88}O_{0.12}$. A similar result was obtained for 1150°C sample. However, the amount of NbO was decreased at this lower temperature. The diffraction peaks of NbO almost disappeared at 1100°C: nearly a single phase, $Nb_2N_{0.88}O_{0.12}$, was obtained at the end of this heating sequence. The peaks of $Nb_2N_{0.88}O_{0.12}$ are indicated by circles in Fig. 1. Figure 2 shows the X-ray diffraction patterns for the samples heated at 1080°C with different reaction periods of 3 and 5 weeks. For 3 weeks, the pattern is similar to that for the 1150°C sample in Fig. 1, indicating that the product was a mixture of two phases. However, the diffraction peaks of NbO wholly vanished after reduction for 5 weeks, i.e., $Nb_2O_{0.88}O_{0.12}$ was obtained in a single phase. The color of the final product was black. The density determined by the toluene displacement method was 8.22 ± 0.06 g/cm^3. Although a definite conclusion cannot be given, it seems likely
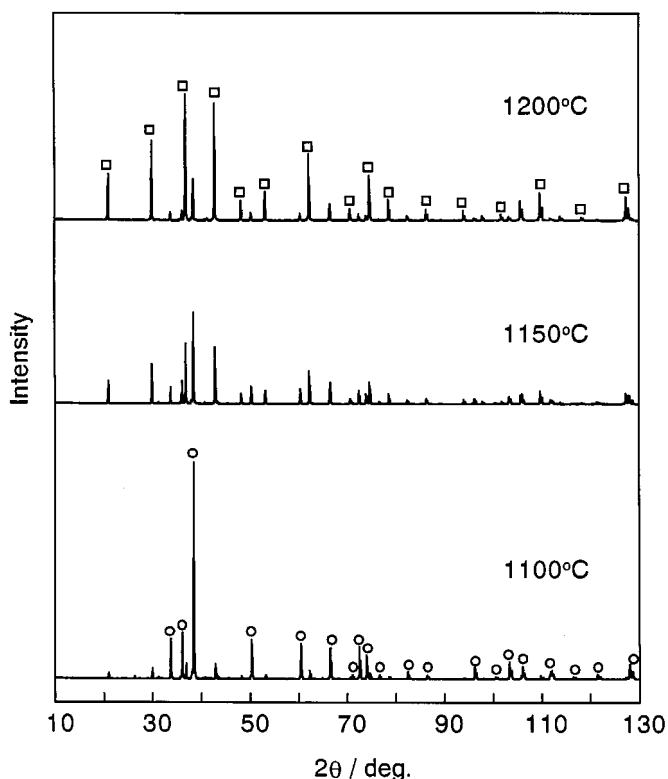
FIG. 1. X-ray diffraction patterns for the products after reduction of Nb_2O_5 at 1200, 1150, and 1100°C: $\square$, NbO; $\bigcirc$, $Nb_2N_{0.88}O_{0.12}$.

that heating temperatures higher than 1100°C are unnecessary for forming $Nb_2N_{0.88}O_{0.12}$. The important factor is possibly a long reaction time with H_2 gas containing N_2. Note that the sample heated at 1080°C for 3 weeks was the mixture of $Nb_2N_{0.88}O_{0.12}$ and a large amount of NbO (Fig. 2), but additional heating for 2 weeks resulted in formation of $Nb_2N_{0.88}O_{0.12}$ in a single phase.

On oxidation of the $Nb_2N_{0.88}O_{0.12}$ phase in air, the color of the powder changed from black to pink-white at 600°C, and finally to white at 800°C. The product heated up to 800°C was identified as a single phase of β-Nb_2O_5 by powder X-ray diffractometry. From the weight increase of this reaction and the results of the Kjeldahl method, the x and y values in $Nb_2N_xO_y$ were calculated to be $x = 0.883$ and $y = 0.125$, respectively, as the average of three determinations. This results showed that the product was expressed as $Nb_2N_{0.88}O_{0.12}$. The average valence of niobium in $Nb_2N_{0.88}O_{0.12}$ was found to be 0.48 ± 0.11 by the cerium back-titration method. Although the experimental error was not so small, it is reasonable to say that the bonding in $Nb_2N_{0.88}O_{0.12}$ was not of typical ionic nature.

Crystal Structure of $Nb_2N_{0.88}O_{0.12}$

The X-ray powder pattern of $Nb_2N_{0.88}O_{0.12}$ is shown in Fig. 3 by a dotted line. The peak profiles refined by Rietveld

calculation are shown as a solid line in the same figure. First, all diffraction lines were indexed on the basis of hexagonal structure. In the AB_2 crystals with hexagonal CdI_2 structure, the A and B atoms are known to occupy the $1a$ and $2d$ positions of $P\bar{3}m1$, respectively. For $Nb_2N_{0.88}O_{0.12}$, the d-spacing and the diffraction intensities were calculated by the LAZY-PULVERIX program assuming that the Nb atoms occupy the $2d$ position and the N/O atoms occupy the $1a$ position. The calculated peaks were found to be basically in agreement with the observed peaks. However, it was revealed by detailed investigation that several small peaks (26.3, 43.4, and 56.1°) in the observed pattern could not be assigned to the $P\bar{3}m1$ space group. These small peaks could also not be explained by the crystal structure of Nb_2N with space group $P6_3/mmc$, which is the NiAs type of structure with the nitrogen occupancy in the $2a$ position of 0.5 (16).

The space group which consistently represents the present crystal structure was $P\bar{3}1m$ of hexagonal system. This structure showed marked similarity to the structure of β-Nb_2N (ε-Fe_2N type) with the space group $P\bar{3}1m$ (17). The oxygen atoms of $Nb_2N_{0.88}O_{0.12}$ are assumed to partly occupy the position of nitrogen in the Nb_2N lattice. In this cell, the nitrogen and oxygen atoms locate two different crystallographic positions, i.e., N(1) and O(1) in the $1a$ position, and N(2) and O(2) in the $2d$ position, respectively. Since no superstructure lines were observed in the diffraction patterns, the arrangement of the nitrogen and oxygen atoms are considered to be statistical in each position. For this statistical case, the lowest reliability factor R_F was also obtained in the Rietveld refinement. Therefore,
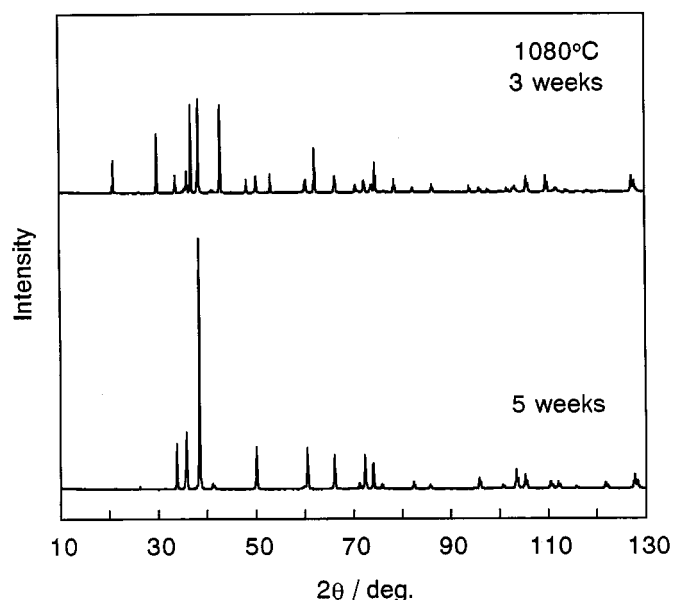

FIG. 2. X-ray diffraction patterns for the products after reduction of Nb_2O_5 at 1080°C for 3 and 5 weeks.
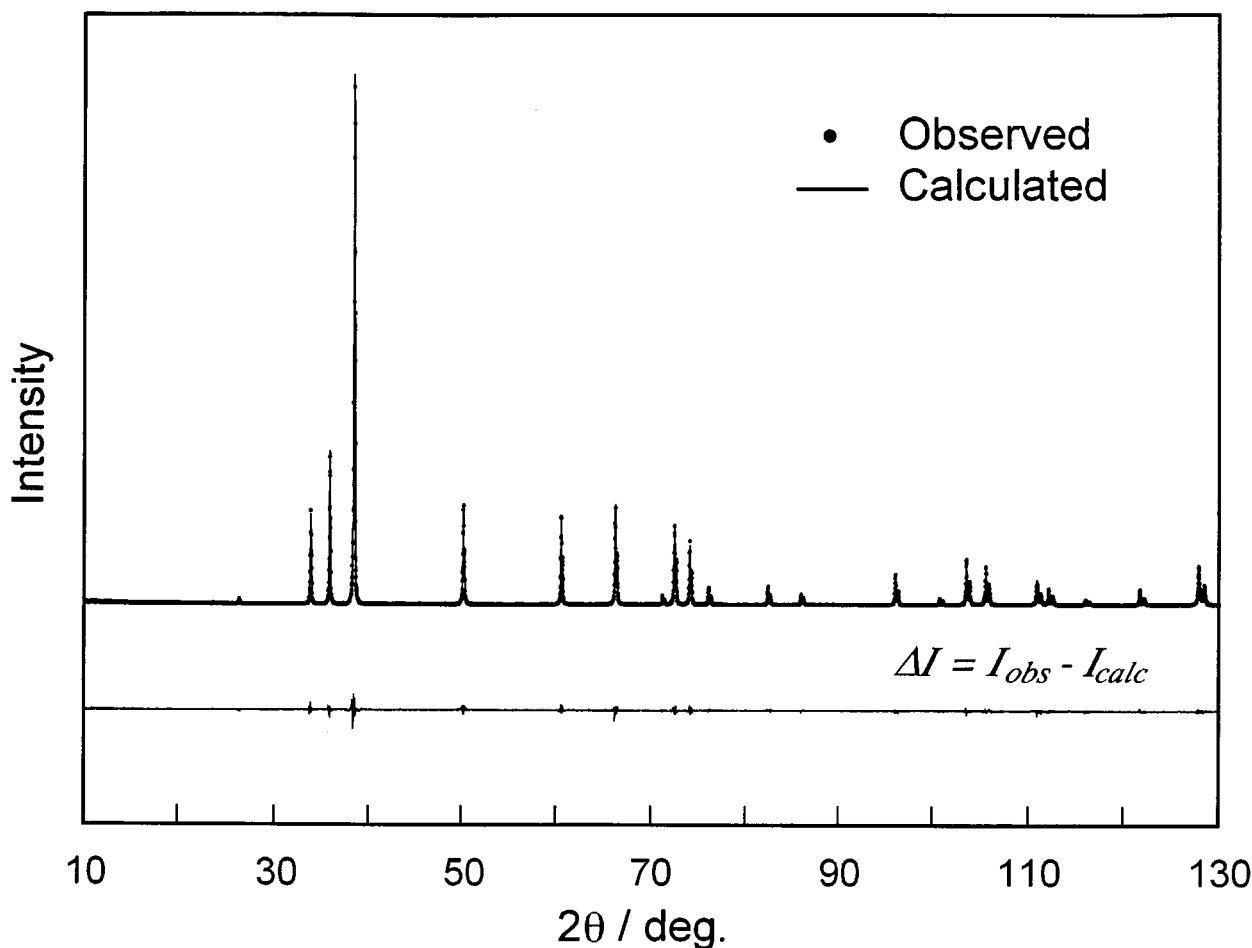
FIG. 3. X-ray diffraction pattern of $Nb_2N_{0.88}O_{0.12}$ together with final Rietveld refinement and difference profiles.

the compound can be regarded as a kind of solid solution of β-Nb_2N and hypothetical Nb_2O. The niobium atoms are located in the $6k$ position. Figure 4 shows the ordered atom arrangement of niobium and nitrogen/oxygen atoms in the x–y plane of the above structure (Fig. 4a) and a perspective view of the unit cell (Fig. 4b), where the niobium and nitrogen/oxygen atoms are shown by small and large circles, respectively. The d-spacings and peak intensities based on the $P\bar{3}1m$ structure were calculated using the LAZY-PUL-VERIX program. For the calculation, the lattice constants and the atom parameters refined by the Rietveld analysis described later were used. The results are listed in Table 1. The calculated d-spacings and integrated peak intensities were found to be in good agreement with the observed ones.

For the refinement by the RIETAN program, the intensities of 24 peaks obtained in the range of $10° \leq 2\theta \leq 130°$ were used. To determine the occupancies of nitrogen and oxygen in the $1a$ and $2d$ positions, the R_F was changed as a function of the occupancy of oxygen in the $2d$ site, $g[O]_{2d}$. The other occupancies were calculated from the chemical composition and the given $g[O]_{2d}$ value. Figure 5 shows the $g[O]_{2d}$ dependence on the R_F value. The minimum R_F value was obtained at $g[O]_{2d} = 0.10$, leading to $g[N]_{1a} = 0.84$, $g[O]_{1a} = 0.16$, and $g[N]_{2d} = 0.90$. The refined crystal data are tabulated in Table 2. The profile fitting in the program was performed by the pseudo-Voigt function. As described in Fig. 3, the calculated peaks are seen to fit satisfactorily the observed peaks. In the figure, ΔI shows the difference in the observed and calculated intensities. The final reliability factors were $R_{WP} = 17.05$, $R_P = 9.70$, $R_I = 1.98$, and $R_F = 3.69\%$. The refined atom positions are listed in Table 3. The refined lattice constants are $a = 5.2916 \pm 0.0001$ and $c = 4.9987 \pm 0.0001$ Å, which are larger compared with the reported values of single-crystal β-Nb_2N, $a = 5.267$ Å and $c = 4.988$ Å (17). With the lattice constants of $Nb_2N_{0.88}O_{0.12}$, the density was calculated to be 8.22 g/cm^3, which is in excellent agreement with the experimental density (8.22 $\pm$ 0.06 g/cm^3) obtained by the toluene displacement method. The refinement of the isotropic displacement parameters was carried out by assuming $B(N) = B(O)$, since
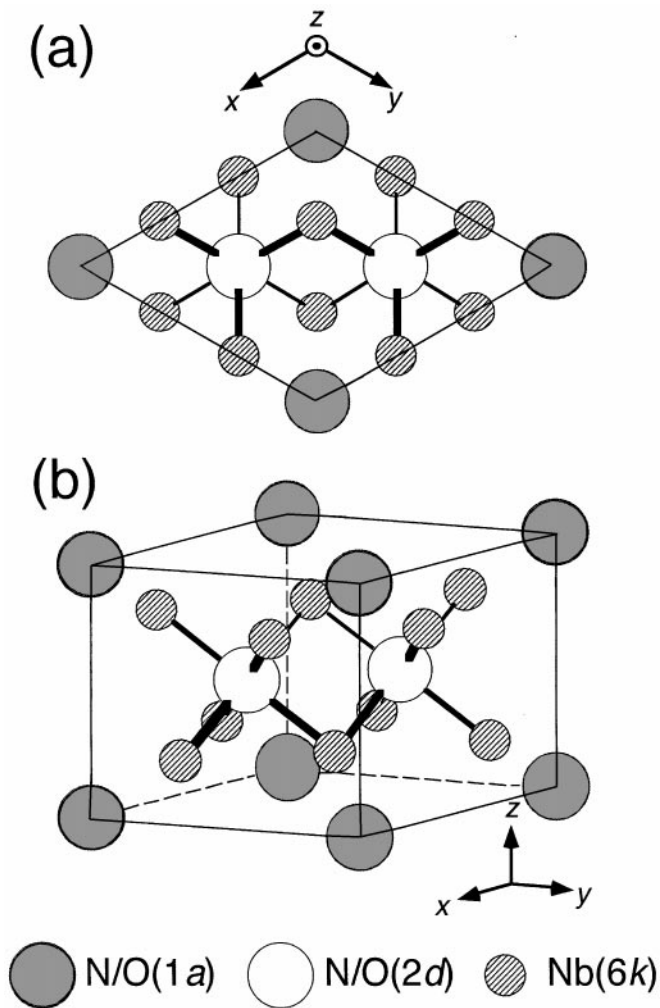
N/O(1a) ◯ N/O(2d) ▨ Nb(6k)

FIG. 4. Schematic representation of the atom arrangement of the niobium and nitrogen/oxygen atoms: (a) view along the c-axis, (b) perspective view.

TABLE 1
Observed and Calculated d-spacings and Integrated Intensities of $Nb_2N_{0.88}O_{0.12}$ (Space Group $P\bar{3}1m$)

h	k	l	d(obs.)	d(calc.)	I/I_0(obs.)	I/I_0(calc.)
1	0	1	3.3833	3.3780	0.9	1.1
1	1	0	2.6482	2.6458	16.9	17.4
0	0	2	2.5007	2.4993	27.3	23.2
1	1	1	2.3399	2.3384	100.0	100.0
2	0	1	2.0833	2.0829	0.2	0.2
1	1	2	1.8179	1.8169	20.5	19.0
2	1	1	1.6370	1.6366	0.1	0.1
3	0	0	1.5281	1.5276	18.3	18.5
1	1	3	1.4101	1.4099	21.4	18.8
2	2	0	1.3232	1.3229	1.8	2.0
3	0	2	1.3036	1.3034	17.6	17.2
2	2	1	1.2790	1.2789	13.4	13.5
0	0	4	1.2498	1.2497	3.5	3.0
2	2	2	1.1694	1.1692	3.9	4.1
1	1	4	1.1301	1.1300	2.6	2.5
2	2	3	1.0360	1.0361	7.7	7.7
4	1	0	1.0000	1.0000	1.9	2.0
4	1	1	0.9806	0.9806	13.8	14.4
3	0	4	0.9673	0.9672	10.6	10.4
1	1	5	0.9352	0.9352	7.1	7.2
4	1	2	0.9285	0.9285	5.1	5.7
2	2	4	0.9083	0.9084	2.0	2.1
3	3	0	0.8819	0.8819	5.2	5.6
4	1	3	0.8574	0.8574	16.6	16.8

phase $Nb_2N_{0.88}O_{0.12}$ obtained above. If the substitution of oxygen by nitrogen in the $Nb_2N_{0.88}O_{0.12}$ took place successively, the lattice constants would have approached those
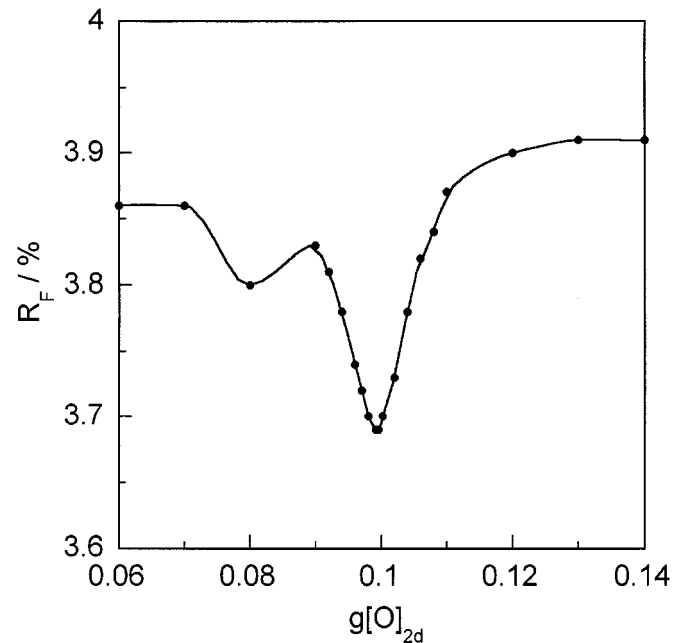
the atomic scattering factor of nitrogen is close to that of oxygen, and nitrogen and oxygen atoms locate randomly in the same planes of the $Nb_2N_{0.88}O_{0.12}$ crystal. The isotropic displacement parameters of niobium and nitrogen/oxygen are 0.18 ± 0.01 and 0.52 ± 0.17 $Å^2$, respectively. The refined positional parameters x and z of niobium at the $6k$ site are 0.333 ± 0.001 and 0.248 ± 0.001, respectively. The z value shows a small deviation from the ideal position $z = 1/4$. From these results it was concluded that the structure of $Nb_2N_{0.88}O_{0.12}$ is explained by the hexagonal system having space group $P\bar{3}1m$.

The lattice constants of the $Nb_2N_{0.88}O_{0.12}$ phase in the two-phase mixture of NbO and $Nb_2N_{0.88}O_{0.12}$ obtained by heating at 1150 and 1100°C (Fig. 1) were calculated to be $a = 5.2917$ Å, $c = 4.9985$ Å and $a = 5.2917$, $c = 4.9982$ Å, respectively, by using the LAZY-PULVERIX program. These values are close to the lattice constants of single-

FIG. 5. Effect of $g[O]_{2d}$ on the R_F value obtained by Rietveld refinement.

TABLE 2
Crystal Data for $Nb_2N_{0.88}O_{0.12}$

Color	black
Crystal system	hexagonal
Space group	$P\bar{3}1m$ (no. 162)
Z	3
Lattice constants	$a = 5.2916 \pm 0.0001$ Å
	$c = 4.9987 \pm 0.0001$ Å
Cell volume	121.22 Å^3
Formula weight	200.06
Calculated density	8.22 g/cm^3
R_{wp}	17.05%
R_p	9.70%
R_I	1.98%
R_F	3.69%

TABLE 4
Interatomic Distances between the Closest Atoms in $Nb_2N_{0.88}O_{0.12}$

Atoms	$d_{obs.}$ (Å)
Nb–N(1)/O(1)	2.156 ± 0.001
Nb–N(2)/O(2)	2.167 ± 0.001
Nb–Nb	3.044 ± 0.001–3.075 ± 0.001

of β-Nb$_2$N with heating. However, the scattering of lattice constants was small between the two-phase product and the single-phase one. Therefore, Nb$_2$N$_{0.88}$O$_{0.12}$ is supposed to be a stable composition in the present experimental atmosphere.

Table 4 shows the interatomic distances of Nb–N(1)/O(1), Nb–N(2)/O(2), and Nb–Nb atoms of the compound. In the crystal, each nitrogen/oxygen atom is surrounded by six niobium atoms. These atoms form a trigonal-antiprism. Around each niobium atom, three nitrogen/oxygen atoms are coordinated. The interatomic distances of Nb–N(1)/O(1) are close to those of Nb–N(2)/O(2); i.e., the Nb–N(1)/O(1) and Nb–N(2)/O(2) distances are 2.156 ± 0.001 and 2.167 ± 0.001 Å, respectively. These values are much larger than the interatomic distances of Nb–N (1.98 Å) and Nb–O (2.04 Å), calculated using the interatomic distances of Nb metal, N$_2$ gas, and O$_2$ gas. These interatomic distances are for the covalent/metallic bonding. On the other hand, the Nb–N ionic distance can be calculated with some assumptions. Since the crystal radii are O^{2-}(CN3) = 1.36 Å and O^{2-}(CN6) = 1.40 Å (18), that of N^{3-}(CN3) is estimated to be 1.42 Å from the literature data of N^{3-}(CN6) = 1.46 Å (18). Using the crystal radii data of Nb^{5+}(CN6) = 0.64, Nb^{4+}(CN6) = 0.68 and Nb^{3+}(CN6) = 0.72 Å (18), the crystal radius of Nb$^{1.5+}$(CN6) = 0.78 Å was extrapolated. Then, the combination of Nb$^{1.5+}$(CN6) and N^{3-}(CN3) yields the interatomic distance 2.20 Å, which is in accord

with the measured distances. However, the average valence of niobium was not between 1.0 and 1.5 but was as small as 0.48 ± 0.11, obtained from chemical analysis. The situation is somewhat complicated, but the crystal is likely to be not wholly ionic; it has a significant covalent and/or metallic nature.

CONCLUSION

A new niobium oxynitride, Nb$_2$N$_{0.88}$O$_{0.12}$, has been synthesized in a single phase by reducing Nb$_2$O$_5$ in a stream of H$_2$ containing N$_2$ at 1080°C for 5 weeks. From the powder X-ray diffractometry, it was found that the compound is hexagonal with space group $P\bar{3}1m$ and $Z = 3$. The lattice parameters are $a = 5.2916 \pm 0.0001$ Å and $c = 4.9987 \pm 0.0001$ Å. The nitrogen and oxygen atoms are statistically distributed in the anion sublattices; i.e., Nb$_2$N$_{0.88}$O$_{0.12}$ is regarded as a solid solution of β-Nb$_2$N and hypothetical compound Nb$_2$O. The niobium atoms occupy the $6k$ position with atom parameters $x = 0.333 \pm 0.001$ and $z = 0.248 \pm 0.001$, while the N(1)/O(1) and N(2)/O(2) atoms occupy $1a$ and $2d$ positions, respectively. After the Rietveld refinement, the R_F value of 3.69% was obtained. The isotropic displacement parameters of niobium and N/O were 0.18 ± 0.01 and 0.52 ± 0.17 Å^2, respectively. In the crystal, the N/O atom is surrounded by six niobium atoms forming a trigonal-antiprism. The niobium atom is coordinated by three N/O atoms. The crystal is likely to be not wholly ionic, but it has a significant covalent and/or metallic nature.

TABLE 3
Positional and Thermal Parameters of $Nb_2N_{0.88}O_{0.12}$

Atom	Site	g	x	y	z	B (Å^2)
Nb	6k	1.0	0.333 ± 0.001	0.0	0.248 ± 0.001	0.18 ± 0.01
N(2)	2d	0.84	1/3	2/3	1/2	0.52 ± 0.17
O(2)	2d	0.16	1/3	2/3	1/2	0.52 ± 0.17
N(1)	1a	0.90	0.0	0.0	0.0	0.52 ± 0.17
O(1)	1a	0.10	0.0	0.0	0.0	0.52 ± 0.17

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