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Niobium–aluminum oxynitride prepared by ammonolysis of oxide precursor obtained through the citrate route

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ABSTRACT

Oxynitrides in the $(Nb_{1-x}Al_x)(O,N)$ quaternary system were prepared by ammonolysis of oxide precursor obtained through the citrate route. The products at 1000 °C were a mixture of Nb(N,O) and $NbN_{0.95}$ at the niobium end ($x = 0$) and amorphous Al(O,N) at the aluminum end ($x = 1$). A new cubic compound (A) appeared mixed with Nb(N,O) in the compositional range $0.1 \leq x \leq 0.4$. Its almost pure product was obtained at $x = 0.5$. The X-ray diffraction pattern was rock salt type $(Nb_{0.56}Al_{0.44})(O_{0.38}N_{0.37}\square_{025})$ in F_{m-3m} with $a = 0.43481(1)$ nm. The product showed superconductivity with $T_c = 15$ K. Its crystallinity was much improved and its superconducting volume fraction increased to 32% after its thermal annealing at 1100 °C in evacuated sealed tube. A second cubic compound (B), rock salt type $Nb[(O,N)_{0.85}\square_{0.15}]$ with $a = 0.434$ nm, was observed mixed with amorphous Al(O,N) in the as-prepared products of the range $0.6 \leq x \leq 0.9$.

1. Introduction

Oxynitrides are a group of compounds attracting recent interest for new applications and scientific investigation. Many kinds of oxynitrides have been prepared in the last decades and their applications are also developing. Their crystal chemistry has been extensively reviewed and their properties were related to the role played by nitrogen [1–3]. The substitution of O^{2-} with N^{3-} was assumed to introduce the cross-substitution of M^{2+} with M'^{3+} or the creation of anion vacancy as well as more covalent character [4]. The kinds of oxynitrides are still very limited compared with those of oxides. Their interesting properties also have been studied; dielectric properties [5], basic catalysis [6], chemical sensors [7], oxynitride glasses [8] and so on. The research for their application has been started. Sialon and aluminum oxynitrides can be doped with rare-earth elements for use as phosphor materials in white LED applications [9,10]. Oxynitrides of niobium or tantalum are of current interest as photocatalysts for visible lights [11–13], catalysts for hydroprocessing [14], and non-toxic pigments [15]. The crystal structure, optical, and dielectric properties have been reported for oxynitride perovskites with alkaline earth ions in their A sites [16,17]. The perovskite phase was obtained alone only for lanthanum, due to the size of this cation. From Nd to Gd, the ammonolysis leads to the existence of both pyrochlore and perovskite phases, while with the smaller rare earth Ho, Er, Yb, Y a competition between defect fluorite and perovskite structure-types occurs. The perovskite phase is generally more stable at temperatures higher than that of the formation of pyrochlore and defect fluorite structures [18,19].

The perovskite structure is formed with larger A-site ions such as rare-earth and alkaline earth ions than tantalum ion. Niobium oxynitrides of rock salt type $Mn_{0.54}Nb_{3.07}N_{4.40}O_{0.60}$ with ordered metal vacancies and $MnNb_2(N,O)_3$ with Nb_5N_6-type structure have also been reported as ammonolysis products from mixtures of manganese acetate and niobium xerogel [20]. The latter compound was observed to form trigonal prismatic niobium oxynitride layers interleaved with octahedral layers containing both Mn and Nb. $Li_{16}Nb_2N_8O$ prepared from a mixture of Li_3N, Nb_2O_5, and NbN crystallized into an anti-fluorite-type superstructure [21].

Niobium nitrides form hexagonal close-packed unit cells with the following dimensions [22]: NbN with $a = 0.2956$ nm, $c = 1.1275$ nm; $NbN_{0.95}$ with $a = 0.294$ nm, $c = 0.546$ nm; an interstitial solid solution of $NbN_{0.4}$ with $a = 0.3056$ nm, $c = 0.4956$ nm and $NbN_{0.5}$ with $a = 0.3048$ nm, $c = 0.4995$ nm. $NbN_{0.87-0.94}$ has a rock salt structure with $a = 0.439$ nm and $NbN_{0.75-0.79}$ has a tetragonally deformed version of this structure. Niobium oxynitrides, $NbN_{\sim 0.9}O_{\sim 0.1}$, have a rock salt type structure with lattice parameters in a range of $a = 0.4390$–0.4373 nm. The oxynitride with more anion vacancy, $NbN_{\sim 0.6}O_{\sim 0.3}$ have tetragonally deformed versions. Nitrogen-rich nitrides have also been reported in reaction-deposited thin films: tetragonal Nb_4N_5 with $a = 0.6873$ nm, $c = 0.4298$ nm and hexagonal Nb_5N_6 with

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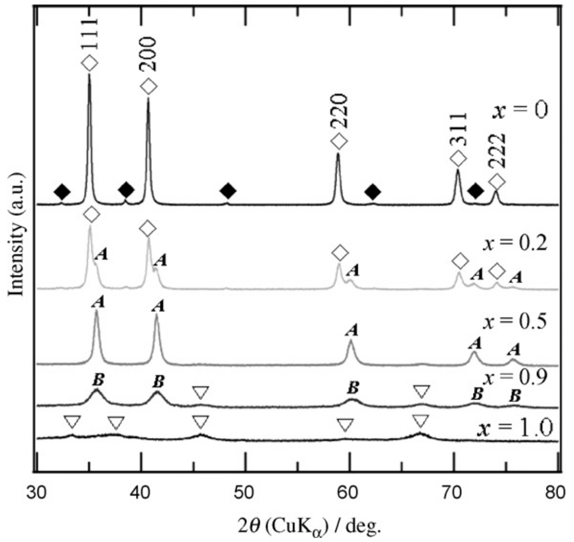

Fig. 1. X-ray diffraction patterns for the $Nb_{1-x}Al_x$ oxynitride products nitrided at 1000 °C. A and B represent diffractions assigned to the new cubic compounds. Open diamonds, triangles and filled diamonds represent diffractions for Nb(N,O), Al(O,N) and $NbN_{0.95}$, respectively.

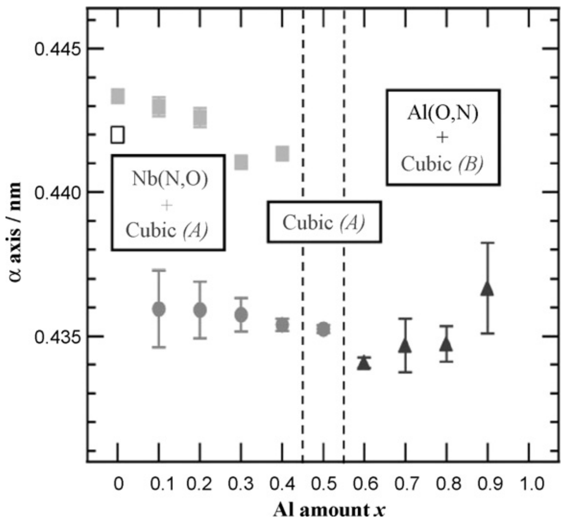

Fig. 2. Variation of cubic lattice parameter a against aluminum amount x. Filled square, circle, and triangle represent values for Nb(N,O) and new cubic compounds (A) and (B), respectively. Open square represents the previously reported value for Nb(N,O) (JCPDS 12-256).

$a = 0.5193$ nm, $c = 1.0380$ nm [23]. Nb_4N_5 and $LiNb_3N_4$ samples have been also prepared as bulk materials [24]. Superconductivity, with $T_c = 17.3$ K, has been reported for niobium nitride having a rock salt structure [25]. Nitrogen rich niobium oxynitride thin films were studied about the effect of composition on superconducting transition temperature [26]. The paper reported the maximum $T_c \approx 13$ K at $NbN_{0.90}O_{0.02}$ without any crystal structure data. The number of report on superconducting quarternary niobium oxynitrides is very limited. Incorporation of nitrogen into $BaNbO_3$ led to superconductivity with $T_c = 22$ K but its exact chemical composition was not known [27].

In the present study, the formation of new oxynitrides was found out in the Nb–Al–O–N quarternary system using ammonolysis of oxide precursors obtained through the citrate route.

2. Experimental

Niobium chloride $NbCl_5$ (Sigma–Aldrich Co., 99.99%) and aluminum chloride hexahydrate $AlCl_3·6H_2O$ (Kanto Chemical Co., 99.9%) were mixed in $(1-x)/x$ molar ratio at 0.1 intervals in the range $0 \le x \le 1$. They were dissolved with an equimolar amount of citric acid (Wako Pure Chemical Co., 98.0%) in 20 ml of ethanol. The solution was heated on a hot plate while stirring to obtain a viscous gel. Oxide precursor was obtained by firing the gel at 350 °C for 1 h in air. After grinding, the sample was nitrided on an alumina boat under an ammonia (Sumitomo Seika Chemical Co., 99.999%) flow of 50 ml/min at 1000 °C for 10 h. Residual ammonia in the furnace tube was purged with high purity argon (Japan Airliquid, 99.999%) after cooling to ambient temperature. An X-ray diffractometer (PANalytical, X'-Pert-MPD) with monochromatized Cu-Kα was used for phase identification and structural analysis. Lattice parameters were refined by a least squares method. Structure refinement was performed using the program RIETAN2000. Oxygen and nitrogen contents were measured by EMGA-620W (Horiba) using Si_3N_4 R003 supplied by the Ceramic Society of Japan and α-Fe_2O_3 reference powder. Magnetic susceptibility and electrical conductivity were measured with PPMS and MPMS-5S (Quantum Design) down to 2 K.

3. Results and discussion

Black product prepared without aluminum was primarily Nb(N,O) (JCPDS 12-256) slightly contaminated with $NbN_{0.95}$ (JCPDS 25-1361), as shown in Fig. 1. The Nb(N,O) had a slightly expanded crystal lattice with $a = 0.4433$ nm, compared to its previously reported value of $a = 0.442$ nm [28]. The present product had oxygen and nitrogen contents of 1.489 wt% and 4.624 wt%, respectively. Another compound (A) with a face centered cubic lattice also appeared in the products prepared in the compositional range $0.1 \le x \le 0.5$. The largest amount of this product was observed at $x = 0.5$ as depicted in Fig. 1. Oxygen and nitrogen contents were 8.303 wt% and 7.519 wt%, respectively. When the nitridation started from a mixture of Nb_2O_5 and α-Al_2O_3 in the corresponding composition, the product was a mixture of hexagonal NbN, Nb(N,O) and α-Al_2O_3. There was no trace of the compound (A). With an appearance of amorphous Al(O,N), a third compound (B) with a face-centered cubic lattice was observed in the compositional range $0.6 \le x \le 0.9$ as depicted in Fig. 1. Its degree of crystallinity decreased and the proportion of the amorphous Al(O,N) increased with increasing aluminum amount x. The product with $x = 1.0$ was amorphous Al(O,N) [10].

The lattice parameter for Nb(N,O) slightly decreased with increasing aluminum content x, as shown in Fig. 2. This change can be partly attributed to the size difference in atomic radii between Nb (0.143 nm) and Al (0.142 nm) [29]. A nearly constant lattice parameter was observed for the new compound (A) in the products obtained in the Al amount of $x = 0.1$–0.5. Crystal structure of the compound (A) was refined on the almost pure product at the Al amount of $x = 0.5$ slightly contaminated with aluminum oxynitride spinel. The niobium and aluminum atoms randomly distributed in 4a and oxygen and nitrogen atoms in 4b sites in space group F_{m-3m}. Literature values for $Al_{2.81}O_{3.56}N_{0.44}$ spinel was used for the aluminum oxynitride impurity and only its amount was refined because its crystallinity was very poor and its amount was very small [30]. The product (A) can be represented as $(Nb_{0.56}Al_{0.44})(O_{0.38}N_{0.37}\square_{0.25})$ using the refined site occupancy and the lattice parameter $a = 0.43481(1)$ nm with $R_{wp} = 7.59\%$, $R_e = 3.46\%$ and $S = 2.1944$ as represented in Table 1. The X-ray pattern of the Rietveld method and the difference curve are shown in Fig. 3. Its refined lattice parameter is $a = 0.4348$ nm in rock salt structure. The cation–anion bond distance (Nb, Al)–(O, N, $\square$) in random distribution is 0.2174 nm, a half of the a-value. The value is shorter than 0.2194 nm for Nb–N in cubic NbN [31] and longer than 0.2105 nm for Nb–O in NbO [32], 0.1927 nm for Al–N in AlN [33] and 0.1947 nm for Al–O in α-Al_2O_3 [34]. The crystal structure of another cubic compound (B) was refined for the product at $x = 0.6$ as a mixture with $Al_{2.81}O_{3.56}N_{0.44}$ spinel. It was assumed as $Nb((O,N)_{0.85}\square_{0.15})$, having a rock salt structure with $a = 0.4343(0)$ nm as shown in Table 2.