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Mixed valent niobium nitrides and oxynitrides resulting from ammonolysis of alkaline niobates

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Abstract

Nitridation of alkaline niobates $MNbO_3$ and MNb_3O_8 (M = Li, Na, K) in flowing ammonia leads to different reaction products depending on the temperature and the considered niobate. Two series of mixed valent NaCl-type oxynitrides are formed in the Li–Nb–O–N system. A complete nitrogen/oxygen substitution can be obtained since the ternary oxide $LiNb_3O_8$ is transformed, without lithium evaporation, into a ternary nitride $LiNb_3N_4$ which has a filled up MoS_2-type structure. Reaction of sodium or potassium niobates with NH_3 results in a total evaporation of sodium or potassium and formation of the binary nitride Nb_4N_5 closely related to the NaCl structure. © 1997 Elsevier Science S.A.

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1. Introduction

A common method of synthesizing nitride-type compounds consists of the thermal reaction of ammonia with oxides [1]. At $T \geq 823$ K, NH_3 decomposes into active species which can both reduce and nitride to form oxynitrides and nitrides. For example, ammonolysis of silica leads to silicon oxynitride Si_2N_2O or to silicon nitride Si_3N_4 depending on the reaction temperature [2,3].

Such a method has been applied to the nitridation of alkaline niobates. In this case, the reactions are more complex because of two main factors: (i) in the presence of a transition metal compound, the reducing effect of ammonia is often preponderant over its nitriding effect; and (ii) evaporation of alkaline metal can occur. Consequently, the results will depend on several parameters, such as the nature of the alkaline element, the stoichiometry of the starting ternary oxide or the nitridation temperature. We present in this paper the behavior of oxides $MNbO_3$ and MNb_3O_8 (M = Li, Na, K) heated in flowing ammonia at temperatures ranging from 800 to 1000°C.

2. Experimental

2.1. Alkaline niobates

The starting ternary oxides $MNbO_3$ and MNb_3O_8 (M = Li, Na, K) were generally prepared by progressive heating in a muffle furnace of appropriate mixtures of reagent-grade niobium oxide and alkaline carbonate or nitrate in the range 900–1200°C. Two cycles of heating with an intermediate grinding were often necessary to obtain X-ray pure phases.

2.2. Ammonolysis

The nitridation reactions were performed by treating oxide powders in flowing non-dehydrated

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commercial ammonia (NH_3 flow rate: 30–40 l h^{-1}) at the desired temperature (heating rate: 10°C min^{-1}).

3. Results

3.1. Ammonolysis of $LiNbO_3$

By holding $LiNbO_3$ powder at 1000°C under ammonia flow, a cubic NaCl-type oxynitride phase is formed, the composition depending on nitridation time: lithium evaporates at the same time as the proportion of nitrogen in the anionic network increases. Its general formula can be written $Li_{2-x}Nb_{2+x}O_yN_{4-y}$ with the two following experimental limit compositions: $Li_2Nb_2O_{1.46}N_{2.54}$ (short nitridation time, $x = 0$) and $Li_{1.69}Nb_{2.31}O_{0.46}N_{3.54}$ (long nitridation time, Li/Nb min = 0.73) [4]. It can be pointed out that the formal oxidation state of niobium atoms keeps a constant value, d_{ox}Nb ~ 4.25, in the whole composition range. The cubic parameter value, which also remains constant, $a = 4.315(1)$ Å (10 XRD lines fitted), corresponds to a random distribution of both cations, Li and Nb, and anions, N and O, in the 4(a) and 4(b) positions of the space groupe $Fm\bar{3}m$.

3.2. Ammonolysis of $LiNb_3O_8$

On the contrary, when $LiNb_3O_8$ powder is heated in flowing ammonia, no loss of lithium is detected whatever nitridation temperature and time. Depending on the chosen reaction temperature, 800°C or 1000°C, a partial or complete nitrogen/oxygen substitution has been observed, with the formation of two types of phases.

At 800°C, a cubic NaCl-type oxynitride phase is prepared, which is different from the preceding one. The general formula is $Li_{1-x}Nb_{3-3x}\square_{4x}O_yN_{4-y}$ (Li/Nb = 1/3; $0.03 \leq x \leq 0.15$, $0.3 \leq y \leq 1.2$), with the systematic presence of cationic vacancies [4]. A maximum nitrogen enrichment has been found for the composition $Li_{0.97}Nb_{2.91}\square_{0.12}O_{0.3}N_{3.7}$ ($a = 4.326(1)$ Å, 10 XRD lines fitted) [5]. Here also the cubic unit cell parameter remains nearly constant along the series of compositions: $a = 4.323$–4.326 Å. It is higher than that of the preceding NaCl-type phase and may be associated to a lower mean value of the niobium formal oxidation state, d_{ox}Nb ≃ 3.85. Moreover, let us note that it is lower than that of the nitride δ-NbN (rock salt structure, $a = 4.3927$ Å [6]), in which d_{ox}Nb is formally equal to 3.

When $LiNb_3O_8$ is reacted with NH_3 above 800°C, a new hexagonal phase appears which, at first, co-exists with the cubic one, as shown by the X-ray diffraction powder patterns of Fig. 1 [5]. The unit cell parameters of this phase (called α) are (21 lines fitted):

$$a_{hex.} = 3.002(1)\ \text{Å} \quad c_{hex.} = 10.34(1)\ \text{Å}.$$

The diffraction peaks of the cubic phase decrease in intensity as the nitridation temperature (or time) increases. However, before their total disappearance a third phase forms (called β) which can be indexed with the hexagonal parameters (28 XRD lines fitted):

$$a_{hex.} = 5.2023(5)\ \text{Å} \quad c_{hex.} = 10.363(1)\ \text{Å}.$$

The unit cell parameters of the β phase are closely related to those of the α phase according to:

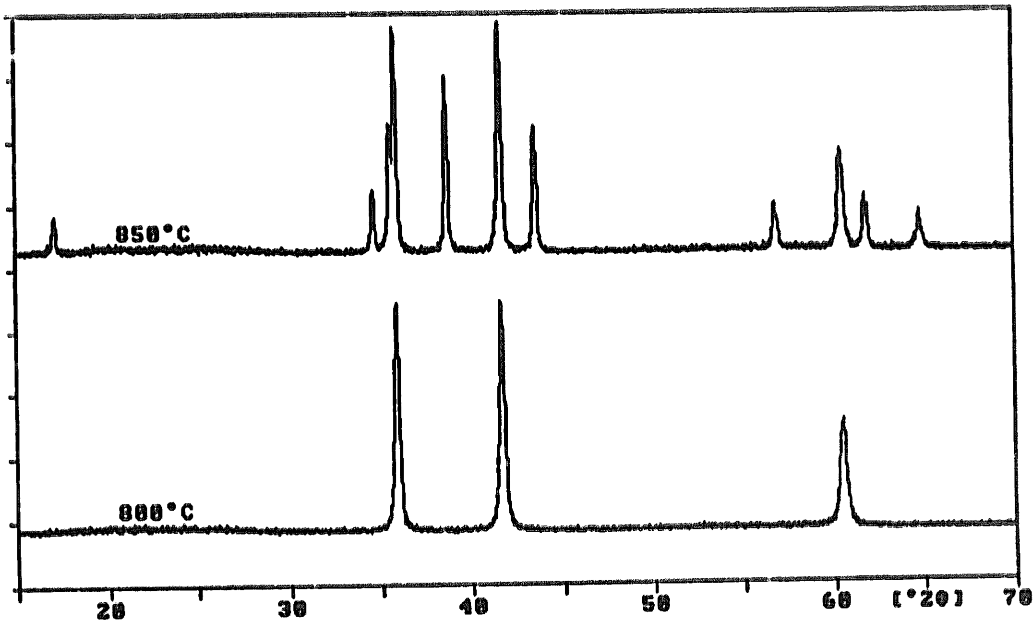

Fig. 1. $LiNb_3O_8 + NH_3$-XRD powder patterns of reaction products at 800°C (cubic Li–Nb–O–N phase) and at 850°C (cubic Li–Nb–O–N phase + hexagonal α-$LiNb_3N_4$).

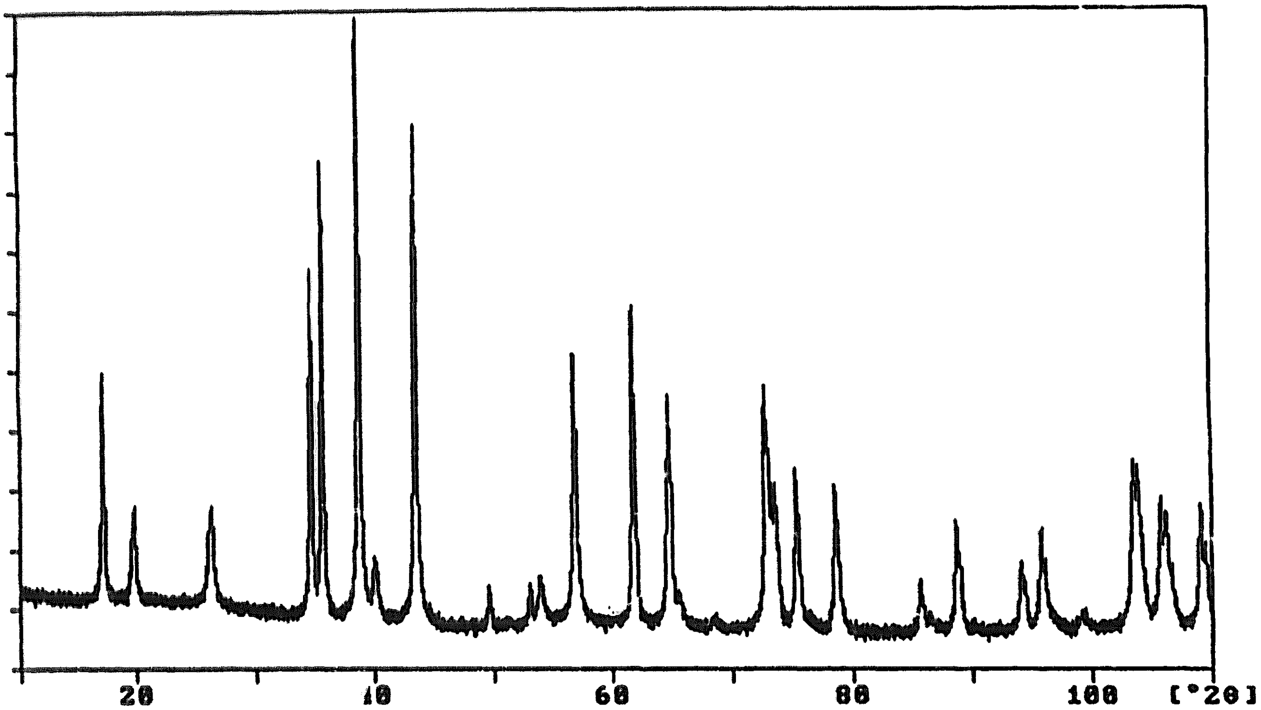

Fig. 2. X-ray diffraction powder pattern of β-$LiNb_3N_4$.

$a_\beta = a_\alpha . \sqrt{3}$

$c_\beta = c_\alpha$

$V_\beta = 3V_\alpha$

Contrary to the α phase which is always in a mixture either with the cubic or with the β phase, the β phase can easily be prepared in a pure state by heating $LiNb_3O_8$ at 1000°C. It has been identified as a ternary nitride $LiNb_3N_{3.7}$ (N wt.% obs. = 15.3_5) showing a slight nitrogen deficiency with respect to a formulation $LiNb_3N_4$ (N wt.% calc. = 16.40) [7]. Fig. 2 shows the corresponding X-ray diffraction powder pattern which only differs from that of the α phase in the presence of additional superstructure peaks. The formal oxidation state of niobium in this nitride is d_{ox}Nb = 3.35.

$LiNb_3N_{4-\varepsilon}$ is isostructural with $Li_{1-x}Ta_{3+x}N_4$ [8] and with Ta_5N_6 (or $\square_{0.67}Ta_{3.33}N_4$) [9]. The crystal structure — space group $P6_3/mcm$; $Z = 3$ — can be described as a filled up 2H-MoS_2-type structure consisting of alternate layers of nitrogen prisms and octahedra: $[Li_3Nb_3]_{(octa.)}Nb_{6(prism.)}N_{12}$. The lithium atoms and the octahedrally coordinated niobium atoms are partially ordered in the 2b and 4d positions of the space group. Fig. 3 shows the atom arrangement in the unit cell.

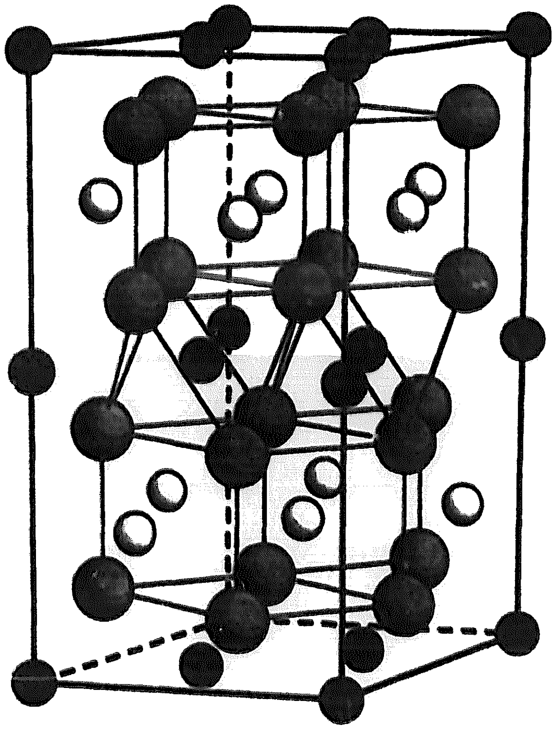

Fig. 3. β-$LiNb_3N_4$ unit cell showing nitrogen prisms and octahedra (large spheres); prismatic Nb atoms, white spheres; octahedral (Li + Nb) atoms, black and dark grey spheres.

The α phase, which can be formulated $LiNb_3N_{4-\varepsilon}O_\varepsilon$ ($Z = 1$), has the same structure as the ternary nitride $BaCeN_2$ [10]. In comparison with the β phase, the structural arrangement is characterized by a random distribution of the Li and octahedrally surrounded Nb atoms in the 2(a) position of the space groupe $P6_3/mmc$. The presence of a small amount of oxygen in the α phase is corroborated by the fact that the $\alpha \rightarrow \beta$ transformation is essentially influenced by the nitridation time and not only by the temperature.

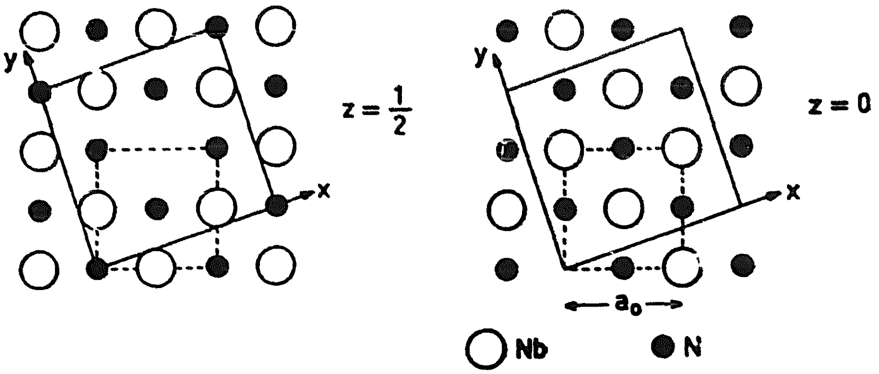

Fig. 4. Views of the Nb_4N_5 structure along [001] at $z = 0$ and $z = 1/2$.

Moreover no $\beta \rightarrow \alpha$ transformation has been observed.

3.3. Ammonolysis of MNb_3O_8 and $MNbO_3$ (M = Na, K)

The niobates $NaNb_3O_8$ and KNb_3O_8 are decomposed by ammonia at 550–600°C to give a mixture of the corresponding $MNbO_3$ niobate and a Nb(O,N) oxynitride phase of NaCl-type ($a = 4.31$ Å).

Direct ammonolysis of sodium or potassium niobate $MNbO_3$ at 800°C results in a total evaporation of sodium or potassium with formation of the binary nitride Nb_4N_5 which crystallizes tetragonally (26 XRD lines fitted) with:

$$a = 6.853(1)\ \text{Å}$$
$$c = 4.270(2)\ \text{Å}$$

Nb_4N_5 has a structure closely related to that of δ-NbN (NaCl-type) with niobium vacancies. It is isostructural with Ta_4N_5 [9,11] and Ti_4O_5 [12] — space group $I4/m$, $Z = 2$. Fig. 4 shows the correspondence between the tetragonal unit cell of Nb_4N_5 and the cubic one of δ-NbN. Nb_4N_5 is metallic in character and shows a superconductivity transition at 10 K.

4. Conclusion

Starting from alkaline niobates $MNbO_3$ and MNb_3O_8 (M = Li, Na, K) heated under ammonia flow, several mixed valent binary and ternary niobium nitrides and oxynitrides can be synthesized. In particular, the transformation of the ternary oxide $LiNb_3O_8$ into a ternary nitride $LiNb_3N_4$ is indicative of stability of the lithium–nitrogen bond, already illustrated by Li_3N as the only alkaline binary nitride. Note also that another lithium and niobium oxynitride $Li_{16}Nb_2N_8O$, where niobium is pentavalent, has been recently reported to crystallize in an anti-fluorite superstructure [13].

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