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Monometallic oxynitrides containing transition metals of the groups 5 and 6 starting from freeze-dried precursors

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Abstract

Early transition elements oxynitrides M(OxNy) (M = V, Mo, Cr and W) have been obtained by direct ammonolysis of precursors resulting from the freeze-drying of aqueous solutions of the appropriate metal salts. A study of the influence of the preparative variables on the outcomes of this procedure is presented. Monometallic oxynitrides have been prepared as single phases by direct ammonolysis of the respective freeze-dried precursors at the appropriate conditions (temperature, time and cooling rate). All the compounds have the rock-salt crystal structure, in which the metal atoms are in a face-centred cubic arrangement, with non-metal atoms occupying octahedral interstitial positions. The materials have been characterized by X-ray powder diffraction, elemental analysis and thermogravimetric analysis under oxygen flow.

Keywords: Oxynitride; Transition elements; Freeze drying method

1. Introduction

Transition metal nitrides are of technological importance. They have extreme hardness, excellent corrosion resistance and high temperature stability and have thus found applications as cutting tools [1-9]. Catalysis is one of the application fields stirring up higher interest in the chemistry of the transition metal nitrides [10–12]. Indeed, some monometallic derivatives have proved to be adequate to replace noble metals in a variety of catalytic processes [13]. Oxynitrides of transition metal are examples of promising materials in this field owing to their activity and selectivity in processes like ammonia synthesis [14–16], Fischer–Tropsh reaction [17–21], hydrogenation [22–25], oxidation [26–27], hydrodenitrogenation and hydrodesulfurization [28–32]. The chemistry of metallic nitrides remained for much time unexplored because of limitations imposed by the available preparative techniques. In practice, it was the application of the novel synthetic chemistry which opened new prospects in this seemingly residual area. Obviously, it has been during period when a diversity of useful properties and new applications of this class of materials has been evidenced [1]. A major problem with the synthesis of metallic nitrides concerns the large bond energy of the dinitrogen molecule. This implies the need for high temperatures to activate the gas. Under these conditions, the nitridation processes lead to the entropically favoured formation of materials with low nitrogen content. An usually related difficulty comes from the high stability of the monometallic phases. In any case, the need for high temperatures in the direct synthesis of metallic nitrides also is imposed by the slow diffusion velocities of the gas inside the metallic particles. Consequently, a common characteristic of the new synthesis methodologies is the search for alternative reaction path through which the cationic diffusion distances become lowered, thus facilitating the preparation of nitrides at relatively low temperatures [33–36]. In fact, as suggested above, the search for soft procedures (as an alternative to the ceramic method) has been the leitmotiv of many efforts by solid-state chemists in recent times [37–43].

2. Experimental

2.1. Synthesis

Materials used as reagents in this work are NH4VO3 (Fluka, 99.0%), (NH4)6Mo7O24.4H2O (Panreac, 99.0%), (NH4)2CrO4 (Panreac, 99.5%) and (NH4)6W12O39.18H2O (Aldrich, 99.98%). Starting metallic element containing solutions were prepared by dissolving the salts in distilled water. The masses of the different reagents were adjusted to give 5 g of final product. Droplets of these solutions were flash frozen by contact with liquid nitrogen and then freeze-dried at a pressure of 1-10 Pa in a Telstar Cryodos freeze-drier. In this way, dried solid precursors were obtained as amorphous (X-ray diffraction) loose powders.

Oxynitrides were synthesized by ammonolysis of the adequate amorphous precursors. The gases employed were NH3 (99.9%) and N2 (99.9995%). A sample of the selected precursor (ca. 0.5 g) was placed into an alumina boat, which was then inserted into a quartz low-through tube furnace. The back end of the tube furnace was connected to an acetic acid trap and the front end was connected to the gas line or to a vacuum pump. Prior to initiating the thermal treatment, the tube furnace was evacuated in vacuo for 20 min, and then purged for 10 min with N2 and another 20 min with NH3. Several runs under different experimental conditions were also performed in order to determine the appropriate conditions for the preparation of pure samples. The precursor powder was heated at 5 K min-1 to a final temperature (Tf) that was held for a period of time (thold) under flowing ammonia (50 cm3 min-1). Then, the solid was cooled at different variable rates (rc) in the same atmosphere. The different cooling rates were obtained by either turning of the oven and leaving the sample inside (slow, ca. 2 K min-1) or by quenching at room temperature (fast, ca. 50 K min-1). After cooling, the product was purged with N2 for 30 min.

2.2. Characterization

The nitrogen content of the oxynitrides was evaluated by standard combustion analysis (Carlo Erba EA 1108); N_2 and CO were separated in a chromatographic column, and measured using a thermal conductivity detector. The oxygen content was indirectly determined by thermogravimetric analysis (Perkin Elmer TGA 7 system). Indeed, the samples were heated under oxygen until complete oxidation ($5Kmin^{-1}$ up to T_{final}, these temperatures being well below the sublimation temperatures of the corresponding oxides). The final products were determined by means of X-ray powder diffraction experiments. The oxygen content was estimated from the observed weight increase, taking into account the nature of the final phases. Summarized in Table 2 are the results of these analyses for the resulting oxynitrides.

X-ray powder diffraction patterns were obtained from a Phillips X'pert automated diffractometer using graphite-monochromated CuKa radiation. In order to reduce preferred orientation, the samples were dusted through a sieve on the holder surface. Routine patterns for phase identification were collected with a scanning step of 0.08° in 2h over the angular range 2h 20-80° with a collection time of 5 s per step. The cell parameters of each product were obtained by profile fitting of the pattern using the method of Le Bail et al. [44] as implemented in the FULLPROF program [45], from patterns collected with a scanning step of 0.02° in 2h, over a wider angular range (2h 20-80°), and with a longer acquisition time (10 s per step) in order to enhance statistics. All graphical representations relating to X-ray powder diffraction patterns were performed using the WinPLOTR [46].

3. Results and discussion

Nitride formation is common to most transition elements. Many compositional and structural forms exist, with many transition elements forming several different nitride phases. In many of these compounds, nitrogen atoms occupy interstitial lattice; for this reason, they are often referred to as interstitial compounds.

Rock salt-type interstitial (with N atoms occupying octahedral sites) crystalline phases, which are tolerant to a certain non-stoichiometry range, have been characterized in each one of the individual V–N, Cr–N, Mo–N and W–N systems. Indeed, the respective compositions for the cubic nitride phases have been given as δ-VN_{1-x} ($0 \le x \le 0.15$-0.20), δ-CrN_{1-x} (with a narrow range of x values), γ-Mo_2N_{1+x} ($-0.2 \le x \le 0.3$) and W_2N [47]. In addition, hexagonal interstitial crystalline phases also have been characterized, with compositions β-V_2N, ε-Cr_2N, δ-MoN and δ-WN (and different homogeneity ranges) [48].

Preliminary treatments for longer times (12 h, to eliminate time as a variable parameter) were carried. In this way, it was possible to evaluate the influence of other key variables in this type of processes, such as the cooling rate. **Figure 1** shows X-ray diffraction patterns of the products resulting from the ammonolysis at 773 to 1073 K of precursors corresponding to V metal composition, when subjected to slow and fast cooling rates.

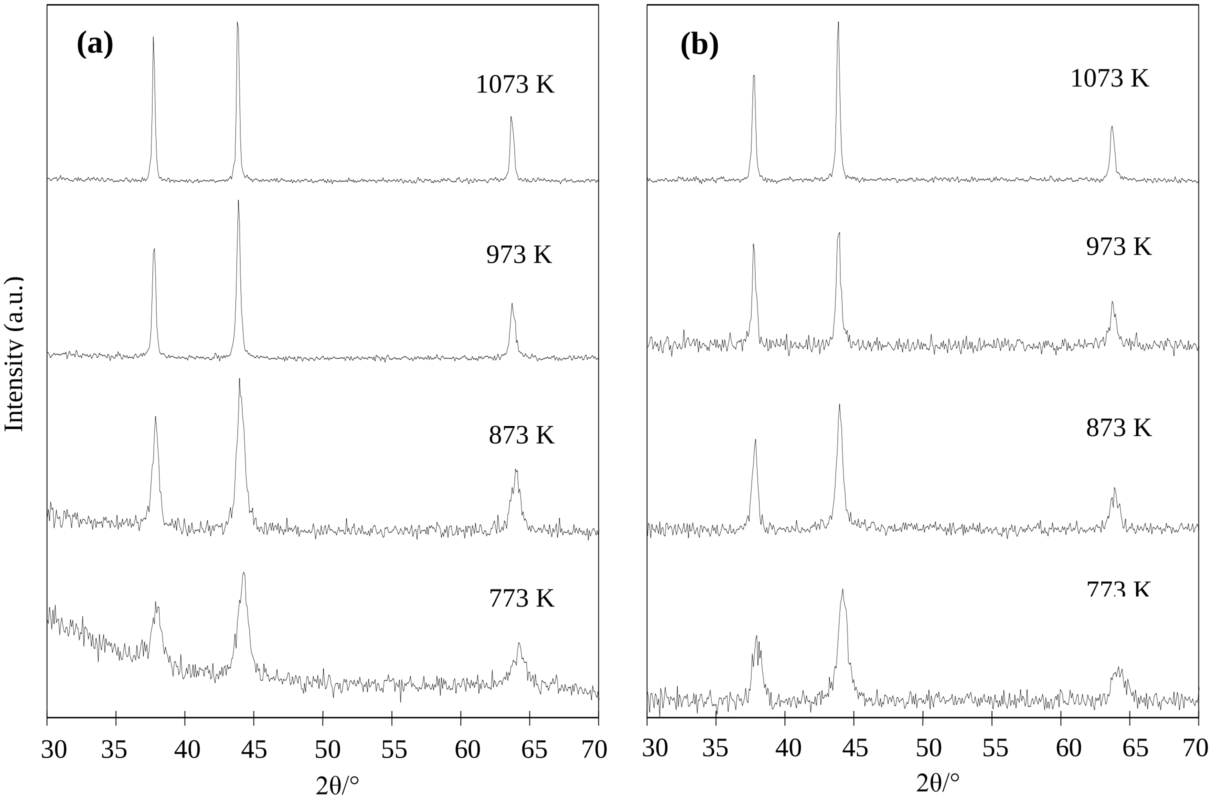

Figure 1. X-Ray diffraction patterns of the products resulting after ammonolysis of the freeze-dried precursor containing only vanadium at different temperatures, after 12 h of thermal treatment and using fast (a) and slow (b) cooling rates.

As can be observed, the cubic phase (δ-VN, JCPDS 35-0768) is obtained as a single phase after nitridation at temperatures as low as 773 K and regardless of the cooling rate.

However, this latter variable (the cooling rate) seems of importance in the case of the molybdenum samples. Thus, slow cooling of samples obtained from 973 to 1073 K **(Figure 2) r**esults in a mixture of the cubic (γ-Mo_2N, JCPDS 25-1366) and hexagonal (δ-MoN JCPDS 25-1367) phases, the relative amount of the cubic phase increasing with temperature. It seems, therefore, that a competition between the cubic and hexagonal phases exists in Mo samples. The hexagonal phase is stabilized at low temperatures, whereas the cubic phase should be stabilized entropically at higher temperatures. Having established the need for quenching in order to stabilize the cubic phase, the influence of the temperature on the nature of the resulting phases was explored in more detail. Figure 2 shows X-ray diffraction patterns of the products that result from the ammonolysis of the precursors corresponding to the Mo metal composition. The effective temperature range is limited for the molybdenum oxynitride. Indeed, at temperatures lower than 973 K, ammonolysis does not occur, and only reduction to MoO_2 (JCPDS 32-0671) is observed. On the other hand, metallic molybdenum (JCPDS 04-0809) is the main crystalline product, together with the cubic phase, when the reaction is performed at 1173 K. Indeed, under these synthetic conditions, cubic molybdenum oxynitride only can be obtained as a single phase in a relatively narrow temperature range, from ca. 973 to 1073 K with fast cooling rate.

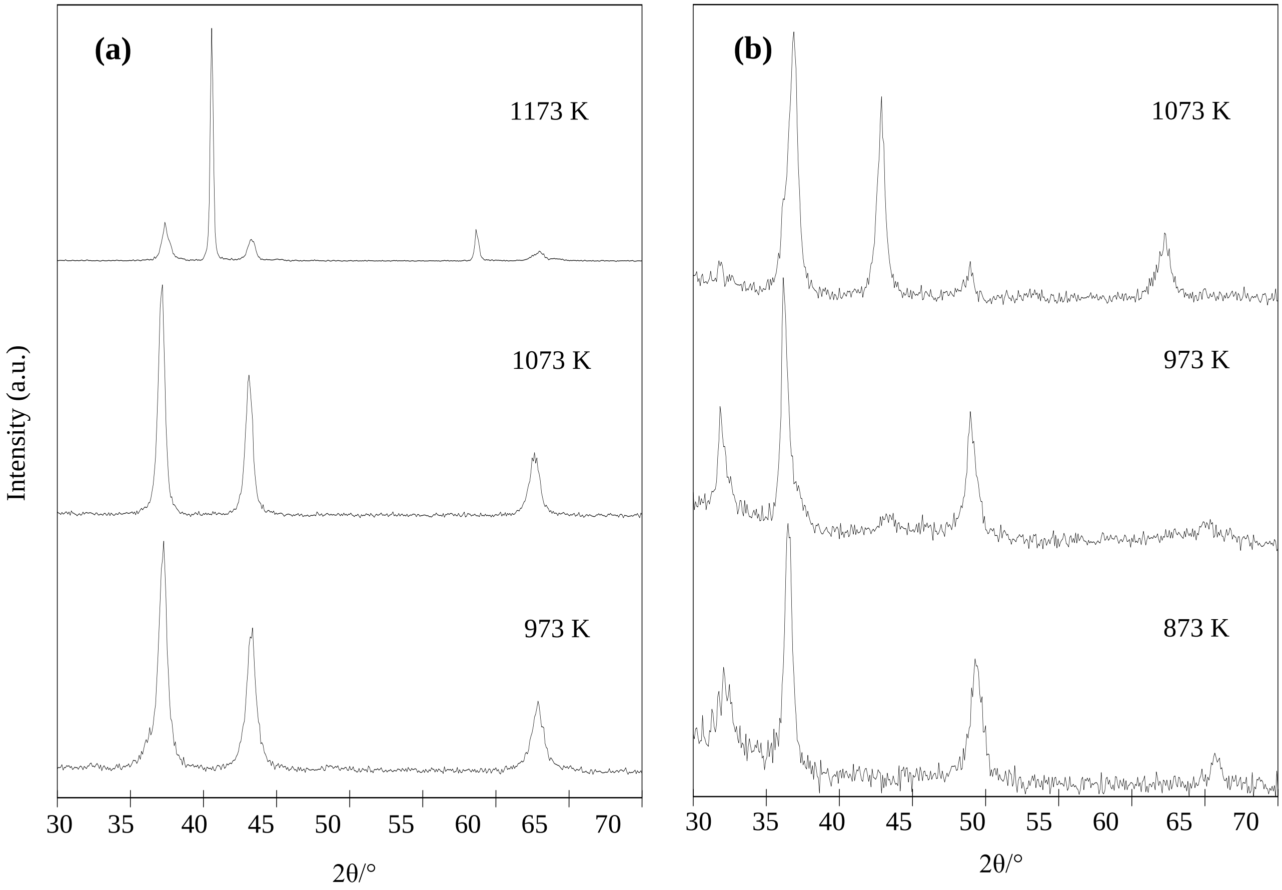

Figure 2. X-Ray diffraction patterns of the products resulting after ammonolysis of the freeze-dried precursor containing only molybdenum at different temperatures, after 12 h of thermal treatment and using fast (a) and slow (b) cooling rates.

Ammonolysis processes on the amorphous solid precursors containing Cr only at long reaction times (12 h) and temperatures ranging from 873 to 1173 K were used. In this way, it was also possible to evaluate the influence of the cooling rate. **Figure 3** shows X-ray diffraction patterns of the products resulting from the ammonolysis process when subjected to a fast cooling rate after treatment at the indicated temperature. As can be observed, the cubic phase (δ-CrN, JCPDS Card 11-0065) is obtained at temperatures between 1023 and 1173 K. At temperatures as low as 1023 K, the Cr_2O_3 (JCDPS 38-1479) is present as an impurity in the product. On the other hand, as occurred for δ-VN, this result is independent of the cooling rate.

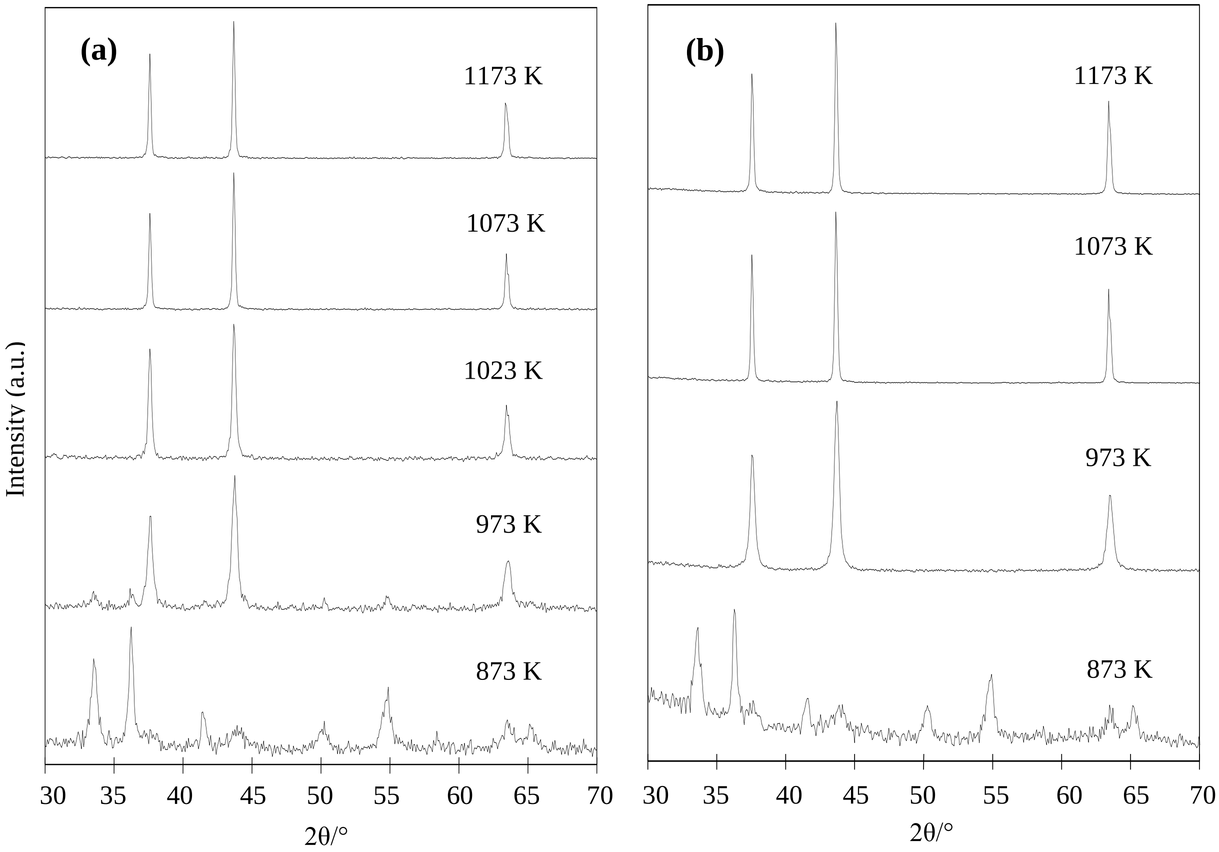

Figure 3. X-Ray diffraction patterns of the products resulting after ammonolysis of the freeze-dried precursor containing only chromium at different temperatures, after 12 h of thermal treatment and using fast (a) and slow (b) cooling rates.

Long reaction times (12 h) and temperatures ranging from 673 to 1173 K were used to optimize conditions for obtaining the W-only containing cubic phase. **Figure 4** shows the X-ray diffraction patterns of the products resulting from the ammonolysis processes when subjected to fast cooling rate after treatment at the indicated temperature. As can be noted, the cubic phase (β-W_2N JCPDS Card 25-1257) is obtained at temperatures as low as 873 K. At lower temperatures (≤ 673 K), WO_2 is obtained (JCPDS Card 32-1393). The cubic phase is obtained pure only in the temperature range 873–973 K. At 1073 K, the majority phase is W metal (JCPDS Card 04-0806) and, at 1173 K, the cubic phase is practically absent. These results are practically independent on the cooling rate. The only difference is that, with a slow cooling rate, the intensity of the cubic phase peaks referred to the W ones is higher, this indicating that W metal ammonolysis occurs at low temperatures. **Table 1** summarizes the synthesis conditions of different metal-only oxynitrides.

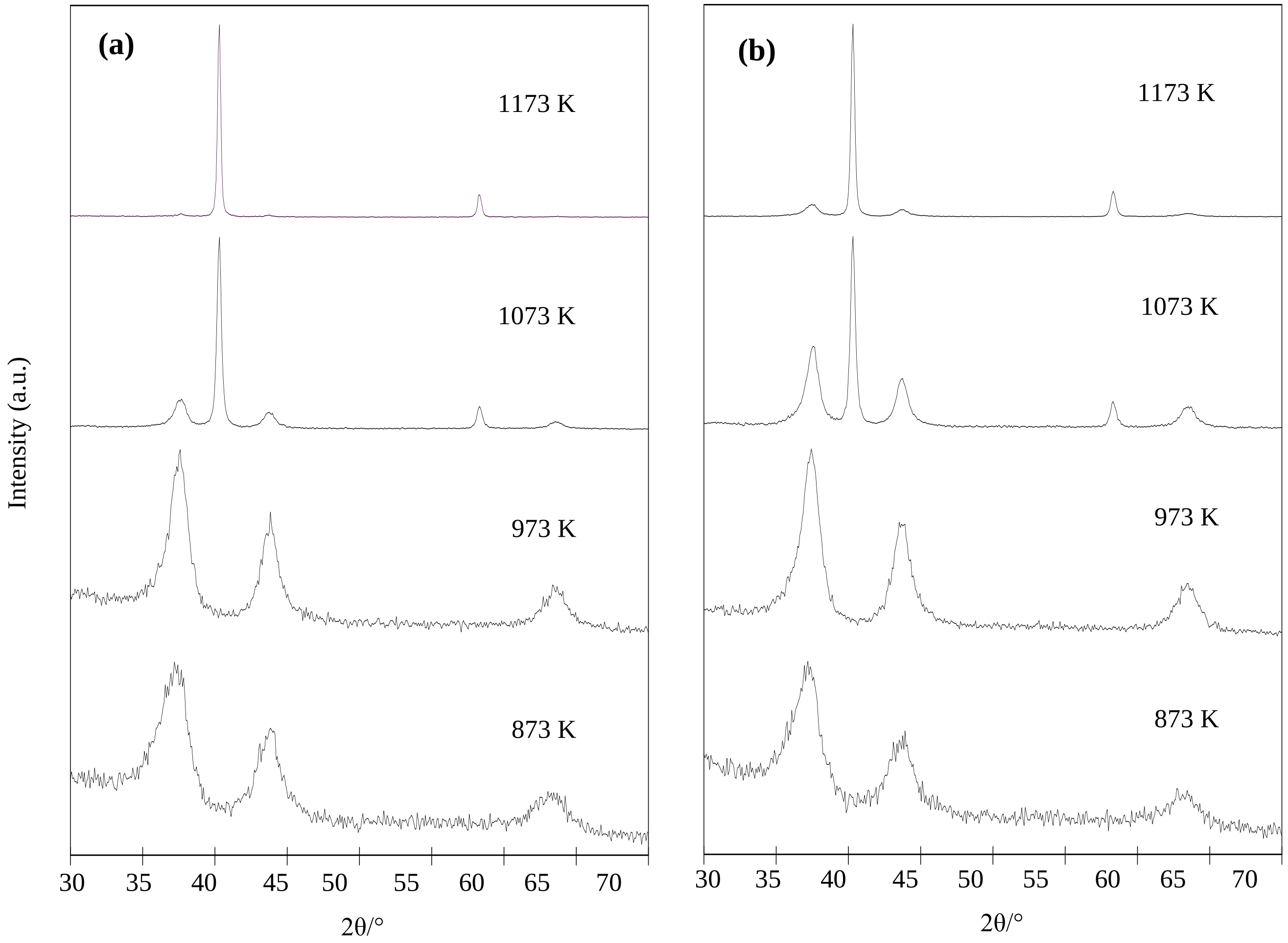

Figure 4. X-Ray diffraction patterns of the products resulting after ammonolysis of the freeze-dried precursor containing only tungsten at different temperatures, after 12 h of thermal treatment and using fast (a) and slow (b) cooling rates.

Samples of studied transitions elements oxynitrides, are characteristic of a rock-salt structure and the cell parameters have been calculated by profile fitting of the patterns, using the LeBail method [44] as implemented in the FULLPROF program [45] (**Table 2**). The size of the crystallites (Table 2) has been calculated from XRD patterns by a standard Scherrer analysis of the half-width of the XRD peaks [48]. Well crystallized $Pb(NO_3)_2$ was used as standard to calibrate the intrinsic width associated with the equipment. Crystallite size are around 37 nm for $V(O_xN_y)$, 15 nm for $Mo(O_xN_y)$, 34 nm for $Cr(O_xN_y)$, and 6 nm for $W(O_xN_y)$).

Table 1. Preparation condition for monometallic oxynitrides

Oxynitride	**Fast cooling rate**		**Slow cooling rate**	
V-(O, N)	873 K	δ-VN	873 K	δ-VN
	973 K	δ-VN	973 K	δ-VN
	1073 K	δ-VN	1073 K	δ-VN
Mo-(O, N)	973 K	γ-Mo_2N	873 K	δ-MoN
	1073 K	γ-Mo_2N	973 K	δ-MoN + minority of γ-Mo_2N
	1173 K	Mo + minority of γ-Mo_2N	1073 K	γ-Mo_2N + minority of δ-MoN
Cr-(O, N)	873 K	Cr_2O_3+ minority of δ-CrN	873 K	Cr_2O_3+ minority of δ-CrN
	973 K	Cubic + minority of Cr_2O_3	973 K	δ-CrN
	1073 K	δ-CrN	1073 K	δ-CrN
	1173 K	δ-CrN	1173 K	δ-CrN
W-(O, N)	873 K	β-W_2N	873 K	β-W_2N
	973 K	β-W_2N	973 K	β-W_2N
	1073 K	W+ minority of β-W_2N	1073 K	W + minority of β-W_2N
	1173 K	W + minority of β-W_2N	1173 K	W + minority of β-W_2N

Table 2. Chemical composition, cell parameters and crystallite size of monometallic oxynitrides

	Oxygen (wt %)	**Nitrogen (wt %)**	**Proposed Stoichiometry**	**Cell Parameter, a (Å)**	**t (nm)**
$Mo(O_xN_y)$	4.2	8.2	$Mo(O_{0.29}N_{0.64})$	4.18188(19)	15
$V(O_xN_y)$	3.1	19.8	$V(O_{0.13}N_{0.93})$	4.13161(9)	37
$Cr(O_xN_y)$	3.5	15.9	$Cr(O_{0.14}N_{0.67})$	4.14439(9)	34
$W(O_xN_y)$	2.2	6.1	$W(O_{0.27}N_{0.87})$	4.1325 (3)	6

Table 2 shows the results of chemical analysis of the resulting products (black powders). The nitrogen content was determined from standard combustion analyses, whereas the oxygen content was indirectly estimated by thermogravimetric analysis. **Figure 5** shows characteristic TGA profiles for the single metal oxynitrides.

The oxidation of the oxynitrides corresponding to the Mo, Cr metal occurs in a two step process. The oxidation begins in all cases at relatively low temperatures (ca. 450-500 K), and is complete between 700 and 900 K, depending on the composition. The final products are MoO_3 (JCPDS 35-0609) and Cr_2O_3 (JCPDS 38-1479). In the case of vanadium and tungsten oxynitrides, the oxidation of the bulk samples occurs in a one step process (ranging from 450–600 to 750–800 K). The final products are V_2O_5 (JCPDS 41-1426) and WO_3 (JCPDS 83-0949). Low temperature oxidation is consistent with the pyrophoric character of these products, which makes passivation necessary. Surface oxidation must account to a great extent for the oxygen content of these oxynitrides.

An interesting result was the observation that the non-metal (N and/or O) to metal molar ratio approaches 1. It seems that, in the presence of oxygen, the fcc array of the metal atoms becomes stabilized respect to the hexagonal phase, and the N and O atoms occupy all the octahedral interstitial positions.

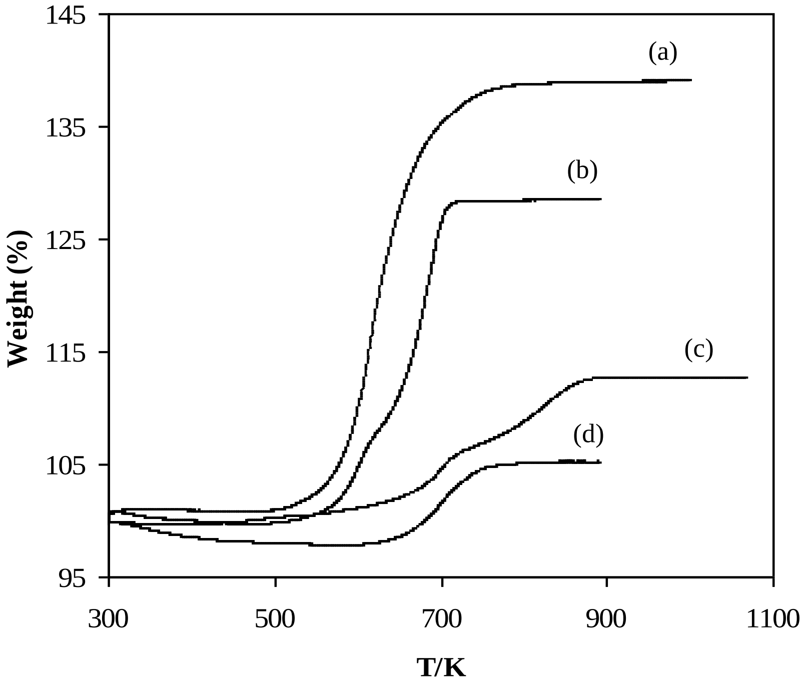

Figure 5. Characteristic TGA profiles corresponding to (a) $V(O_xN_y)$, (b) $Mo(O_xN_y)$, (c) $Cr(O_xN_y)$ and (d) $W(O_xN_y)$

One aspect that deserves some explanation is that concerning the proposed nitrogen and oxygen stoichiometry. Samples tend to be pyrophoric, which is the reason for what they must be passivated (treatment under N_2 atmosphere) prior to their manipulation. The purpose of this passivation is to cover the active surface of the material with a layer of oxide (O_2 present as impurity in N_2) to prevent oxidation of the bulk. Thus, besides the incorporation of oxygen atoms to interstitial positions, which is determinant for stabilizing the cubic structure, surface oxidation should be the main responsible for the high non-metal content that is observed in some products.

Conclusions

Ammonolysis of freeze-dried precursors is an alternative route to synthesize nanopowder transition elements oxynitrides $M(O_xN_y)$ (M = V, Mo, Cr and W) material with the rock salt- type interstitial structure. The synthetic approach reported here could be explored for the optimization of the HDN catalytic properties. Moreover, by starting from aqueous solutions of the metal cations, our approach could open a new way for the preparation of supported HDN oxynitride catalysts.

5. References

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