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Nb−Ta, Nb−Ta−V, and Nb−Ta−Bi Oxides Prepared from Molecular Precursors Based on EDTA

Daisy A. Bayot and Michel M. Devillers*

*Unité de Chimie des Matériaux Inorganiques et Organiques, Place Louis Pasteur 1/3,
B-1348 Louvain-la-Neuve, Belgium*

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Multimetallic oxides of general formula $(Ta_xNb_{1-x})_2O_5$, $Ta_xNb_{1-x}VO_5$, and $BiTa_xNb_{1-x}O_4$ $(0 < x < 1)$ are synthesized by a molecular precursors method from pre-isolated water-soluble EDTA complexes. These materials are obtained by thermal treatment in air of a homogeneous mixture of precursors of the metals to be incorporated in the final oxide. The obtention of a solid solution over the entire range of composition is evidenced, for the three systems studied, by Raman spectroscopy but also by DTA/DSC analyses and powder X-ray diffraction. The incorporation of small amounts of tantalum in the Nb−V−O and Nb−Bi−O systems is shown to stabilize phases difficult to obtain in a pure form, like the $NbVO_5$ and β-$BiNbO_4$ phases. Moreover, the pore size distribution measurements and SEM pictures of the ternary and quaternary oxides reveal the $(Ta_xNb_{1-x})_2O_5$ and $BiTa_xNb_{1-x}O_4$ phases display a disordered porous character. The $Ta_xNb_{1-x}VO_5$ oxides present a high crystallinity.

I. Introduction

In recent years, multimetallic Nb-based oxides have generated considerable interest in many fields because of their attractive physical properties: for example, such oxides are widely studied as ferroelectric and piezoelectric materials such as $BiNbO_4$,[1] or as ion conductors such as Y_3NbO_7.[2] Another important feature of Nb-based oxides is their promising catalytic behavior in several highly challenging industrial processes, such as alkane oxidation or ammoxidation. For instance, pure niobium pentoxide itself is a very selective catalyst for propane oxidative dehydrogenation (ODH) even though its catalytic activity is only moderate.[3] In recent years, it has been shown that associating niobium pentoxide with elements such as V, Mo, or Sb could considerably improve the catalytic activity while maintaining a high selectivity.[4,5] Among these three elements, vanadium was found to be the optimal promoter and the $NbVO_5$ phase is often mentioned in the literature as active for ODH.[6,7] Unfortunately, this mixed oxide can be obtained so far in a pure form only by a sol−gel method.[8]

Within the same context, analogous Ta-based oxides, such as $BiTaO_4$ and $TaVO_5$, were also reported but in a much less extended way than for niobium. The literature describes mainly solid solutions between niobium and tantalum mixed oxides.[9,10] In particular, it was found very recently that associating niobium and tantalum pentoxide in a common lattice produces mesoporous materials.[11] These niobium−tantalum ternary oxides have been prepared by a neutral templating sol−gel route, using the pentachlorides as metal precursors and a block copolymer as template. Moreover, the partial substitution of Nb^{5+} by Ta^{5+} in the $NbVO_5$ and $BiNbO_4$ phases was also reported to lead to oxides of general formula $Ta_xNb_{1-x}VO_5$[12,13] and $BiTa_xNb_{1-x}O_4$[14,15] $(0 < x < 1)$, respectively. In the case of the Nb−Ta−V−O system, the quaternary oxides were synthesized according a sol−gel route using the alkoxides or pentachlorides as metals precursors. In the case of the Nb−Ta−Bi−O system, the materials were prepared most of the time by a solid-state reaction between the Ta^V and Nb^V pentoxides and Bi^{III} carbonate or oxide. This method requires very high temperatures as well as a repeated grinding between the successive calcination steps. An alternative method based on mechanochemical activation of a mixture of Bi_2O_3, Nb_2O_5, and Ta_2O_5 was also reported recently.[14]

The purpose of this work is to synthesize these Nb−Ta-based bulk oxides by using, for the various elements to be incorporated in the final material, pre-isolated

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* To whom correspondence should be addressed. E-mail: devillers@chim.ucl.ac.be. Fax: +32-10-472330.

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molecular precursors in which the metals are surrounded by chelating organic ligands. Ideally, these precursors must be compatible with each other, mainly from the point of view of solubility and thermal degradation scheme. This molecular precursor approach differs quite a lot from the polymeric precursor methods such as citrate or Pechini methods, developed thirty years ago,[16,17] in which different metals are trapped in a gelified citric acid or mixed citric acid/ethyleneglycol network, respectively, without isolating metal complexes characterized by a given stoichiometry. The advantages of precursors methods in general are numerous: (i) their use provides homogeneous materials due to the mixing at a molecular level of the metals;[18] (ii) the presence of chelating organic ligands in the complexes has been shown to avoid unwanted metal segregation during oxide formation;[19] (iii) the precursors route allows formation of crystalline oxides under conditions significantly milder than those employed in conventional solid-state synthesis[20,21] and resulting in materials with relatively high specific surface areas. Next to these two methods, the sol−gel process, also commonly used for the preparation of multimetallic oxides, displays mainly the same advantages but its major drawbacks are the high cost and moisture sensitivity of metal alkoxides, which are the typical precursors in this process. Furthermore, when several metals are involved, the homogeneity of the final material is often limited by the large differences in the hydrolysis and condensation rates of the starting precursors. Compared with the citrate or sol−gel methods, the molecular precursors route, also called “chelate method” when the precursors are chelated complexes, offers the advantage of starting with air-stable compounds displaying a well-established stoichiometry. Up to now, the synthesis of Nb- and/or Ta-based multimetallic oxides from chelate metal precursors has usually been carried out by a “liquid mixing method”, starting from a mixture of separately prepared solutions containing metal salts in the presence of a chelating agent such as EDTA, triethanolamine, or citric or tartaric acids.[22−26] When Nb and/or Ta are involved in the formulation, they are most of the time solubilized as complexes with excess amounts of citric [22,23,26] or tartaric acids,[24,25] or engaged as an oxalate compound.[27,28] The use of soluble NTA (nitrilotriacetic acid) or EDTA-precursors of Nb in H_2O_2 medium has been reported only once, but without any information on the molecular structure of the complexes formed.[29]

When different metals are involved in the oxide formulation, the main advantage of the molecular precursors method is the potential use of heterometallic single-source precursors, when available, which provide a much greater control of the metal stoichiometry in the final oxide.[30,31] This method was already successfully applied to the preparation of Nb- and/or Ta-containing oxides such as the $BiNbO_4$ or $BiTaO_4$ phases made from heteroleptic alkoxide−salicylate complexes.[31,32]

For these reasons, we have chosen to explore the ternary and quaternary oxides of the Nb−Ta, Nb−Ta−V, and Nb−Ta−Bi systems prepared by the chelate method. The coordination compounds selected for that purpose are water-soluble and air-stable mononuclear complexes with polyaminocarboxylate (PAC) ligands which we isolated previously; the syntheses and characterization of the diperoxo[ethylenediaminetetraacetato bis(*N*-oxido)] niobate(V) and tantalate(V) complexes were already reported.[33,34]

II. Experimental Section

Chemicals. The guanidinium (gu) salts of the peroxo-EDTA precursors of Nb^V and Ta^V, $(gu)_3[Nb^V(O_2)_2(EDTAO_2)]\cdot 2H_2O$ and $(gu)_3[Ta^V(O_2)_2(EDTAO_2)]\cdot 2H_2O$ were prepared in aqueous medium by substituting two peroxo groups with the EDTA ligand in the tetraperoxometalate anion, $(gu)_3[M^V(O_2)_4]$ ($M^V = Nb^V$, Ta^V), according to procedures described elsewhere.[33,34] These syntheses were carried out in the presence of excess hydrogen peroxide (35 wt %, Acros) which led to the direct formation of complexes with the bis(*N*-oxide) derivative of the EDTA ligand. The synthesis of the vanadium precursor, $(NH_4)_3[V^V(O)_2(EDTA)]\cdot H_2O$, was adapted from a procedure used by Lee to obtain the PDTA derivative:[35] NH_4VO_3 (5 g, 0.043 mol), H_4EDTA (12.49 g, 0.043 mol), and ammonia (25% solution, 8 mL, 0.12 mol) in distilled water (100 mL) produced a yellow solution which was concentrated under reduced pressure up to a final volume of 50 mL. Addition of ethanol (300 mL) yielded a fine yellow solid which was filtered off, washed with ethanol, and air-dried. The bismuth compound used, $(gu)[Bi^{III}(EDTA)(H_2O)]$, was also obtained according to a reported synthesis:[36] H_4EDTA (3 g, 0.01 mol) was dissolved in boiling water and bismuth oxocarbonate, Bi_2CO_5 (2.61 g, 0.05 mol) was then added. The obtained suspension was refluxed for 6 h until complete dissolution. $(gu)_2CO_3$ (0.92 g, 0.05 mol) was added and the progressive elimination of solvent under reduced pressure provided a white crystalline solid which was filtered off and air-dried.

The chemical structures of the anionic Nb, Ta, V, and Bi complexes are drawn in Figure 1.

Synthesis. The mixed Nb−Ta and Nb−Ta−M (M = V or Bi) oxides were prepared by a chelate method. The detailed preparation scheme is illustrated in Figure 2. The corresponding coordination compounds were dissolved together and simultaneously in distilled water according to the appropriate proportions (Nb/Ta or Nb/Ta/M). Some drops of H_2O_2 were sometimes added to the mixture to facilitate dissolution. The

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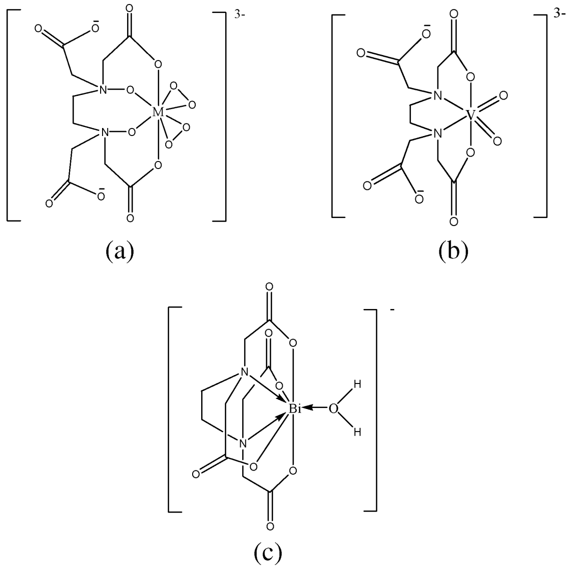

Figure 1. Chemical structures of the various anionic complexes used for the preparation of the mixed oxides: (a) $[M(O_2)_2(EDTAO_2)]^{3-}$ (M = Nb or Ta), (b) $[V(O)_2(EDTA)]^{3-}$ and $[Bi(EDTA)(H_2O)]^{-}$.

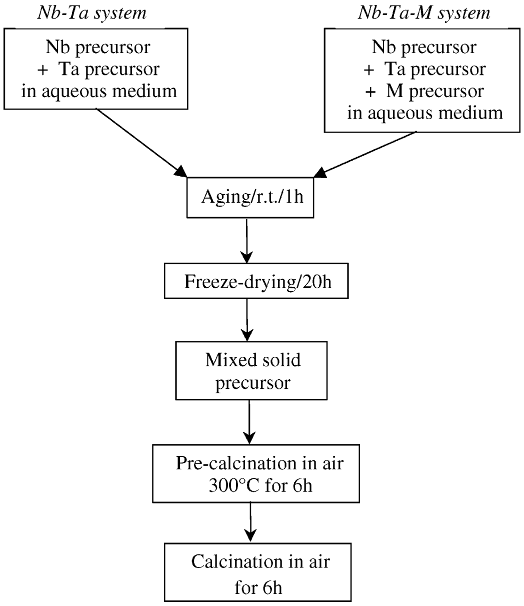

Figure 2. Preparation scheme of the mixed Nb−Ta and Nb−Ta−M oxides (M = V, Bi).

resulting clear solution was then stirred at room temperature during 1 h. The solvent was gently eliminated by a freeze-drying process for 20 h and a mixed solid precursor was then obtained. Various molar ratios were engaged. For the Nb−Ta system, the Nb/Ta proportions considered were 0:1, 0.1:0.9, 0.3:0.7, 0.5:0.5, 0.7:0.3, 0.9:0.1, and 1:0. In the case of the Nb−Ta−M (M = V or Bi) systems, the following Nb/Ta/M compositions were used: 0:1:1, 0.25:0.75:1, 0.5:0.5:1, 0.75:0.25:1, and 1:0:1. The amount of M is constant and the ratio (Nb+Ta)/M is always equal to 1.

The resulting mixed solid precursor was precalcined at 300 °C for 6 h in air, yielding an amorphous material which was then calcined for 6 h in air. The calcination temperatures used were 700 or 800 °C for the Nb−Ta system, depending on the Ta content, and 600 °C for Nb−Ta−M (M = V, Bi) systems and selected according to the thermal behavior.

Safety. Care should be exercised when heating these peroxo-type precursors. Removal of solvent upon heating on vacuum should be avoided. The successive use of the "soft" freeze-drying process to eliminate the solvent first, followed by a precalcination step processed in an oven at a relatively moderate temperature (300 °C), is preferable for safety reasons.

Table 1. Final Decomposition Temperature (T_F) of the $(Ta_xNb_{1-x})_2O_5$ Precursors in Air (heating rate 10 °C min^{-1})

x	0	0.1	0.3	0.5	0.7	0.9	1
T_F/°C	625	640	665	695	720	745	765

Analysis. Differential thermal analysis (DTA) and thermogravimetry (TG) were performed in air at the heating rate of 10 °C min^{-1} using a Mettler Toledo TGA/SDTA851^e analyzer. Differential scanning calorimetry (DSC) analyses were carried out on a Mettler Toledo DSC20 in air at the same heating rate. FT-Raman spectra were recorded on a Bruker spectrometer (type RFS100/S) at the wavelength of 1064 nm. Powder X-ray diffraction (XRD) was carried out on a SIEMENS D-5000 diffractometer using the Cu Kα radiation. Surface areas were measured with a Micromeritics ASAP 2000 analyzer with nitrogen at 77 K and using the Brunauer−Emmet−Teller (BET) method. The pore-size distribution was determined by the Barrett−Joyner−Halenda (BJH) method on the same equipment, and considering the desorption branch of the N_2 sorption isotherm. The scanning electron microscopy (SEM) images were obtained on a DSM982 GEMINI microscope with 1 kV accelerating voltage.

III. Results and Discussion

Nb−Ta−O system. The TG analyses of the solid Nb−Ta precursors obtained by the freeze-drying process show a multistep decomposition into the final oxide up to a final temperature which depends on the Nb/Ta molar ratio. The final decomposition temperature, given in Table 1, actually increases with the Ta content. The DTA of these mixed precursors display several exothermal peaks below 700−750 °C, corresponding to the degradation process, as well as a small peak which coincides with the last step in the TGA and accounts for crystallization. The crystallization temperature of the different samples with various Nb/Ta molar ratios increases with the Ta content. Moreover, a linear and continuous change of this crystallization temperature is observed which is indicative of the homogeneous mixing of the two metal oxides.

The X-ray diffraction studies of the calcined Nb−Ta samples show that the considered thermal treatment applied to the precursors leads to crystalline materials for all compositions. Figure 3 allows comparison of the XRD pattern of the oxide characterized by a 0.5:0.5 Nb/Ta molar ratio with those of the corresponding binary oxides. The similarity of the diffractograms suggests that these compounds are isostructural with orthorhombic Nb_2O_5 (JCPDS file 30-0873), with only slight shifts in 2θ values being observed for several diffraction peaks. The evolution of the lattice parameters with the composition is illustrated in Figure 4. Some overlapping phenomena affect the most intense peaks (see Figure 3). For example, the *180* and *001* reflections, well separated on the diffractogram of Nb_2O_5, are too close to each other in the case of the oxides $(Ta_xNb_{1-x})_2O_5$ with $x = 0.5$ and 1 to be observed as two peaks. The same observation can be done for the *080* and *201* reflections. The a, b, and c values were therefore calculated using the *380* ($2\theta \approx 51°$), *0160* ($2\theta \approx 50°$), and *001* ($2\theta \approx 22°$) lines, respectively, and considering the orthorhombic symmetry reported in the JCPDS file of Nb_2O_5. When the tantalum content increases, we observe that a

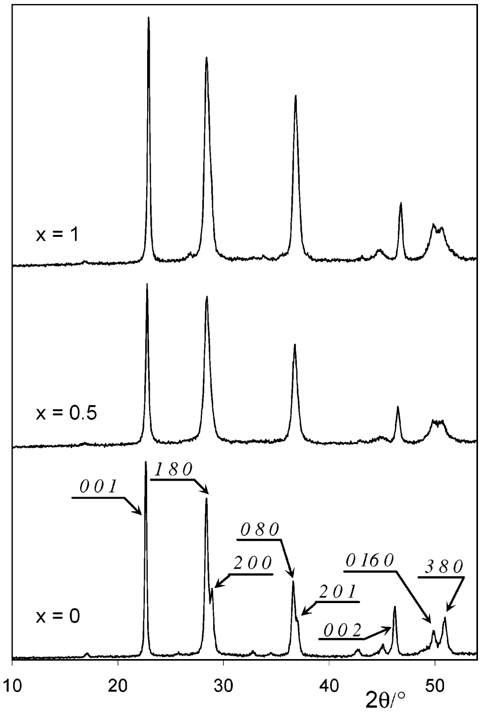

Figure 3. X-ray diffraction patterns of the $(Ta_xNb_{1-x})_2O_5$ mixed oxides ($x = 0, 0.5, 1$).

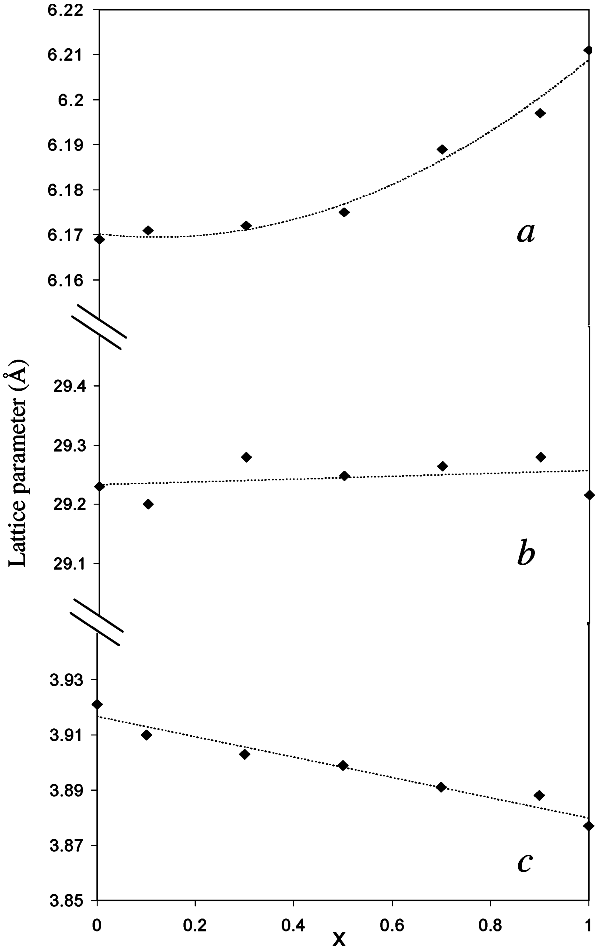

Figure 4. Evolution of the lattice parameters vs the amount of tantalum in the $(Ta_xNb_{1-x})_2O_5$ oxides.

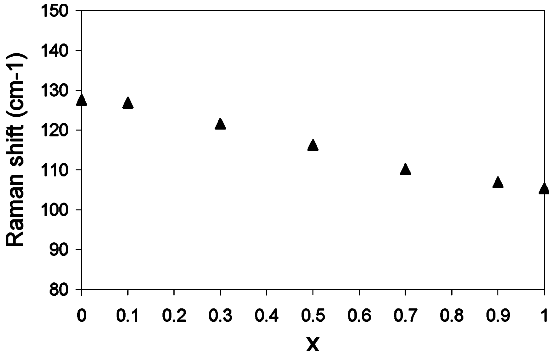

Figure 5. Evolution of a Raman shift (cm^{-1}) vs the amount of tantalum in the $(Ta_xNb_{1-x})_2O_5$ oxides.

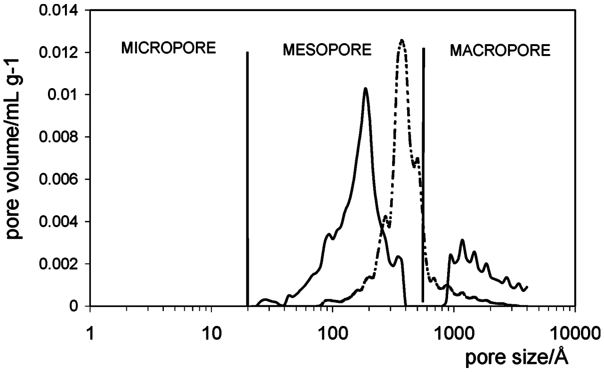

Figure 6. BJH pore-size distribution of the $(Ta_xNb_{1-x})_2O_5$ mixed oxides with $x = 0.5$ (straight line) and $x = 0.3$ (dashed line).

Table 2. BET and BJH Measurements Data of the $(Ta_xNb_{1-x})_2O_5$ Mixed Oxides

x	BET surface area ($m^2\ g^{-1}$)	mean pore size[a] (nm)	pore volume (mL g^{-1})
0	17	45	0.17
0.1	28	34	0.20
0.3	16	36	0.11
0.5	32	19	0.14
0.7	10	26	0.05
0.9	12	41	0.10
1	17	30	0.11

[a] The mean pore size is estimated from the BJH analysis in desorption branch of the N_2 sorption isotherm.

increases regularly, and *c* decreases linearly, while *b* remains almost constant. A similar trend of the lattice parameters evolution was previously evidenced [9,10] but cannot be rationalized on the basis of the respective ionic radii of Nb^{5+} and Ta^{5+}, which are identical (0.74 Å),[37] as a consequence of the so-called "lanthanide contraction". However, these observations strengthen the idea that the ternary oxides have been synthesized as single $(Ta_xNb_{1-x})_2O_5$ phases corresponding to a continuous series of solid solutions between Nb_2O_5 and Ta_2O_5.

The Raman analyses of the Nb−Ta oxides confirm the obtention of solid solutions because (i) the Raman spectra are all similar, and (ii) we observe a linear variation of the position of several Raman bands with the composition (Figure 5). When the Ta content increases, these bands are shifted to lower wavenumbers, in line with the fact that Ta is heavier than Nb. The Raman bands associated with this behavior are therefore assumed to correspond to vibrational modes of metal/oxygen bonds influenced by the local environment.

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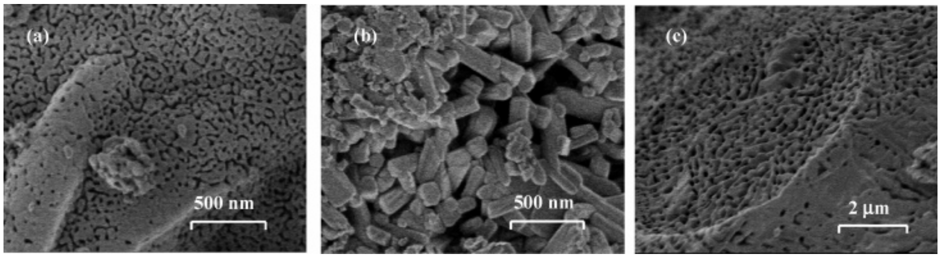

Figure 7. SEM images of the (a) $(Ta_xNb_{1-x})_2O_5$ ($x = 0.9$), (b) $Ta_xNb_{1-x}VO_5$ ($x = 0.5$), and (c) $Ta_xNb_{1-x}BiO_4$ ($x = 0.5$) mixed oxides.

A similar but reverse behavior was previously observed for solid solutions appearing in the HfO_2−ZrO_2 system.[38]

BET, BJH, and SEM measurements have been used to study the morphology and porosity of the samples prepared. The specific surface areas of the Nb−Ta−O oxides are relatively high, varying from 10 to 30 $m^2\ g^{-1}$. A BJH analysis of the desorption curve revealed that the pore size is in the mesopores domain and varies from 15 to 40 nm according to the different compositions. Moreover, the pore size distribution is rather uniformally distributed like, for instance, for the 0.5:0.5 and 0.7:0.3 Nb/Ta compositions (Figure 6). The results of BET and BJH measurements are given in Table 2.

On the SEM image of the oxide characterized by the Nb/Ta composition of 0.1:0.9 (Figure 7a), the sample exhibits a porous character,with the average pore size measured on this image being in good agreement with that obtained from the BJH method. Similar images were obtained for the other compositions, leading to the same conclusions.

Nb−Ta−V−O System. TG analyses of the Nb−Ta−V−O mixed solid precursors display a multistep decomposition into the final oxide, with a final temperature slightly varying with the composition between 460 and 490 °C. DSC analyses were carried out and they gave us information about the crystallization temperature of our oxides. These analyses display an exothermic peak in the region 450−600 °C, which can be assigned to the crystallization process. As shown in Figure 8a, the single crystallization peak appears for the samples of compositions $x = 0.25$, 0.5, and 0.75 at 485, 523, and 558 °C, respectively. These temperatures are intermediate between those observed for the ternary oxides $NbVO_5$ and $TaVO_5$ (470 and 589 °C, respectively), which confirms the formation of a quaternary phase by heating the corresponding precursor. Actually, just like the Nb−Ta−O system, the crystallization temperature of the samples with various Nb/Ta molar ratio increases linearly with the Ta content (Figure 8b).

The X-ray diffraction patterns of $Ta_xNb_{1-x}VO_5$ ($x =$ 0.25, 0.5, 0.75), obtained after crystallization at 600 °C, are very similar to those obtained for the ternary oxides, confirming once again the formation of one single quaternary oxide phase. However, for the sample with $x = 0$, the XRD pattern displays the presence of $NbVO_5$, but together with small amounts of the $Nb_{18}V_4O_{55}$ and V_2O_5 phases. This result is not unexpected because, as said above, $NbVO_5$ has only been obtained up to now via a sol−gel method. However, we showed that it is possible to stabilize the $NbVO_5$ phase by incorporating tantalum in the unit cell, even in a very small amount. We evidenced this behavior by incorporating 1, 2, or 3 molar percents of tantalum in the niobium oxide network ($x = 0.01$, 0.02, and 0.03). Moreover, the position of the diffraction peaks in the XRD patterns of these oxides is very close to that obtained for the ternary oxides, in agreement with the analogy between the ionic radius of Nb^{5+} and Ta^{5+}. Although the main diffraction lines are slightly shifted with the Nb/Ta composition, no regular evolution with the metal content was observed. In that case, Raman spectroscopy provided a more convenient technique to distinguish between a mixture of oxides and a pure solid solution. Just like for the Nb−Ta−O system, the Raman spectra of the $Ta_xNb_{1-x}VO_5$ oxides are all identical and the positions of several Raman bands are also affected by the Nb/Ta composition: a linear decrease of the wavenumber is observed when increasing the Ta content, indicating the homogeneous mixing of the two ternary oxides in a single $Ta_xNb_{1-x}VO_5$ phase.

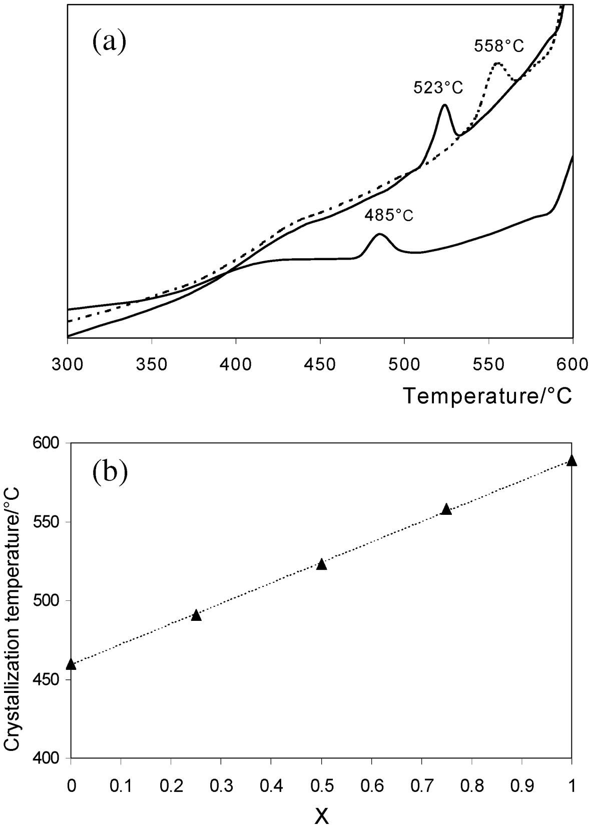

Figure 8. (a) DSC analysis of the $Ta_xNb_{1-x}VO_5$ oxide precursors. (b) Evolution of the crystallization temperature with the amount of tantalum.

The specific surface areas obtained for the Nb−Ta−V−O system are very low (<10 $m^2\ g^{-1}$) in comparison with those obtained for the Nb−Ta−O system. More-

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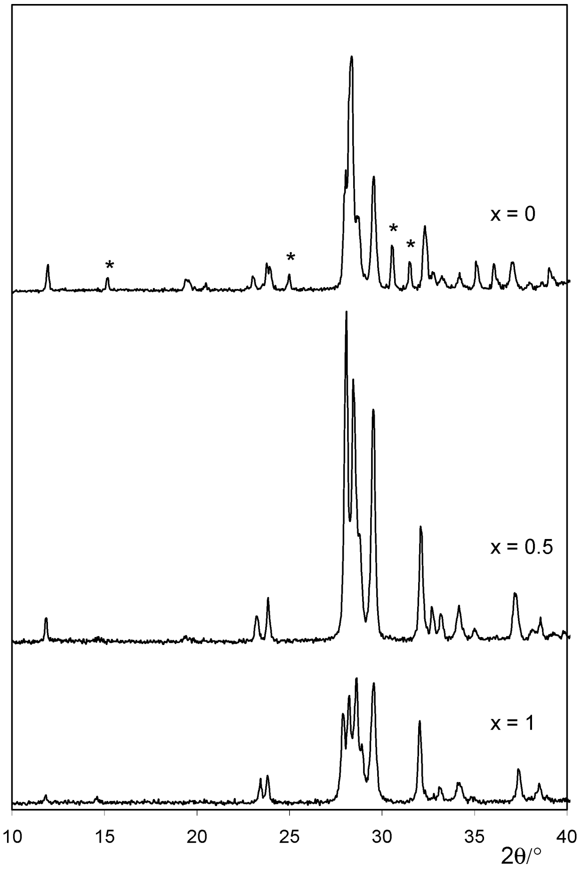

Figure 9. X-ray diffraction patterns of the $Ta_xNb_{1-x}BiO_4$ mixed oxides (x = 0, 0.5, 1). The presence of the α-$BiNbO_4$ phase in the sample with x = 0 is indicated by asterisks. The other lines correspond to β-$BiNbO_4$.

over, the BJH measurements revealed these materials display no porous character at all.

The SEM analyses confirm these results. The morphology of the $Ta_xNb_{1-x}VO_5$ oxides is completely different from that of the $(Ta_xNb_{1-x})_2O_5$ samples. No porosity is observed on the images and the oxides are highly crystalline. As an example, the SEM image of the composition $x = 0.5$ is illustrated in Figure 7b, evidencing some quite large crystallites.

Nb−Ta−Bi−O System. The TG analyses of the mixed Nb−Ta−Bi−O precursors revealed that the decomposition occurs in three steps to produce the final oxide on heating to approximately 550 °C. DSC studies of these precursors showed essentially a broad exothermic peak (from about 320 to 550 °C) prior to the formation of the final mixed oxide. No isolated crystallization peak was observed; the crystallization process probably coincides with the last degradation step. A similar behavior was observed by Kim et al. in the thermal analyses of peroxo-hydroxide precursors for the preparation of pure lead niobates.[29]

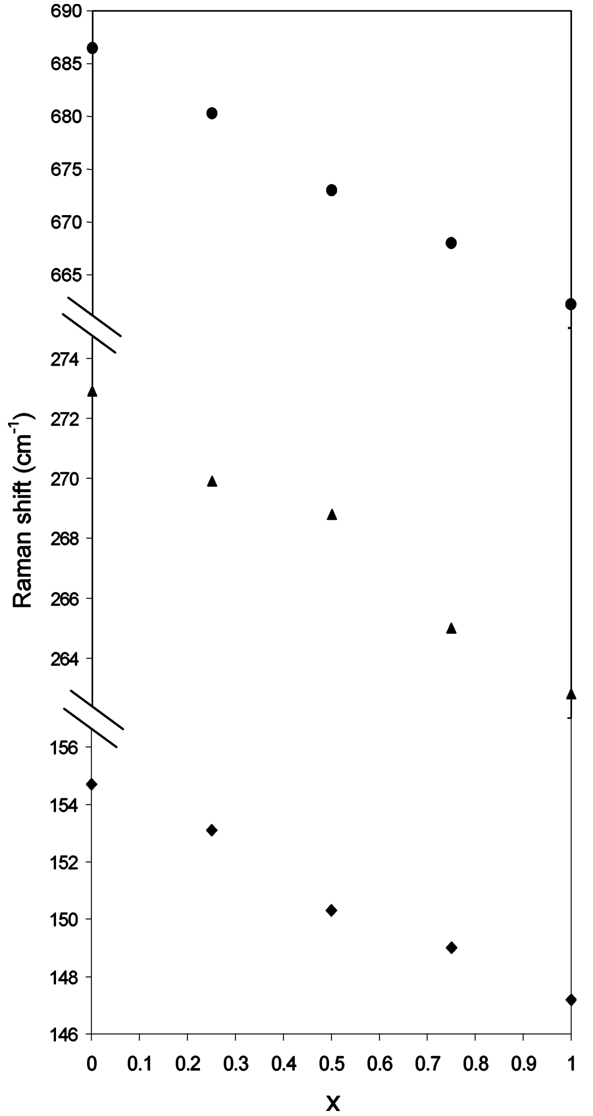

Figure 10. Evolution of three Raman shifts (cm^{-1}) vs the amount of tantalum in the $Ta_xNb_{1-x}BiO_4$ mixed oxides.

Powder X-ray diffraction studies of the $Ta_xNb_{1-x}BiO_4$ oxides calcined at 600 °C during 6 h revealed those materials to be crystalline and single-phased. In all cases, the mixed precursors decomposed on heating in air and the XRD of the final residues were similar to those obtained for the $BiNbO_4$ and $BiTaO_4$ oxides (Figure 9). Only the high-temperature β-phase, which has a triclinic unit cell, was obtained for all compositions except for x = 0, where small amounts of the low-temperature form, α-$BiNbO_4$, were actually detected. When Ta is added ($x > 0$), no trace of α-phase was detected. The incorporation of tantalum in the Nb−Bi−O system is therefore shown to stabilize the triclinic structure. A similar behavior of Ta was described above for the Nb−Ta−V−O system. Moreover, even though the XRD patterns of the $Ta_xNb_{1-x}BiO_4$ oxides are very similar and the position of the diffraction peaks is slightly affected by the substitution degree, no linear correlation with the composition was observed for this system.

Raman spectroscopy provided a stronger evidence for the obtention of a solid solution between $BiNbO_4$ and $BiTaO_4$ than the XRD measurements. The Raman spectra are actually very similar, with a linear variation of the position of several Raman bands with the composition. Just as for the two other systems studied, the different Raman bands are shifted to lower wavenumbers when the Ta content increases, as shown in Figure 10.

The specific surface areas obtained for the Nb−Ta−Bi−O system are also lower than 10 m^2 g^{-1}. The BJH measurements revealed these materials display a partial mesoporous character. A large amount of macropores is actually present.

SEM analyses confirm these results. These materials display an unordered porous character like that of the Nb−Ta−O system, even though the pore size observed on these images is significantly larger in the case of the Nb−Ta−Bi−O system. As an example, the SEM picture for the Nb/Ta/Bi composition 0.5:0.5:1 is illustrated in Figure 7c.

IV. Conclusions

The chelate method starting from peroxo, oxo, and aqua complexes of EDTA has allowed obtention of solid solutions for the systems Nb−Ta−O, Nb−Ta−V−O, and Nb−Ta−Bi−O. The synthesis of the mixed oxides as single phases has been confirmed by Raman spectroscopy and also, most of the time, by X-ray diffraction and thermal analyses. Moreover, the morphology of the samples has been studied by SEM and the pore size distribution was also determined. The $(Ta_xNb_{1-x})_2O_5$ and $Ta_xNb_{1-x}BiO_4$ oxides were shown to display an disordered porous character, while the $Ta_xNb_{1-x}VO_5$ oxides present a high crystallinity. We have also shown that the addition of small amounts of tantalum in the Nb−V−O and Nb−Bi−O systems allows stabilization of phases which are difficult to obtain in a pure form, like the $NbVO_5$ and β-$BiNbO_4$ oxides.

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Supporting Information Available: X-ray diffraction patterns of the $Ta_xNb_{1-x}VO_5$ mixed oxides (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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