Ta$_x$Nb$_{1-x}$VO$_5$ (0 < x < 1) Ternary Oxides: Synthesis by Sol–Gel and Structural Characterization

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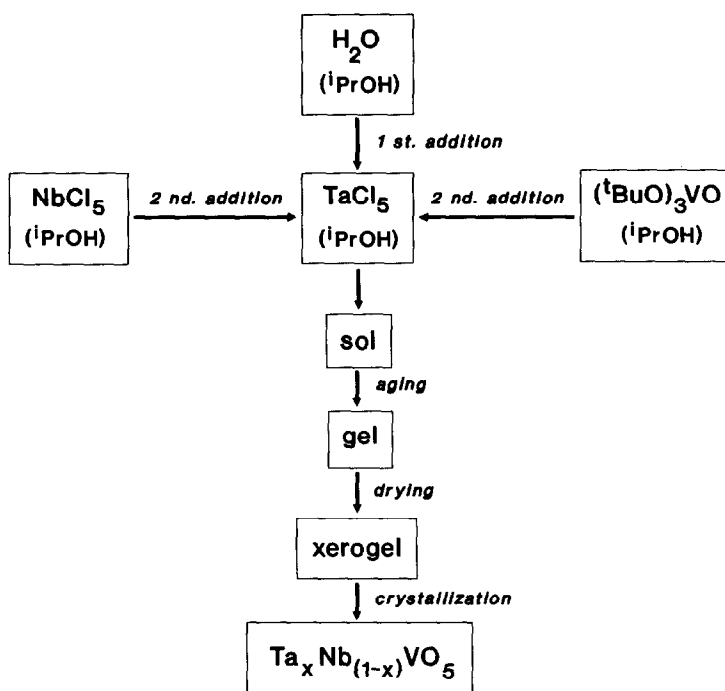
Ternary oxides of general formula Ta$_x$Nb$_{1-x}$VO$_5$ (0 < x < 1) have been synthesized by thermal treatment (873 K, 6 hr) of the corresponding mixed precursor xerogels obtained via sol–gel. The Ta$_x$Nb$_{1-x}$VO$_5$ compounds, characterized by XRD, ED, TEM-EDAX, IR spectroscopy, and chemical and thermal analysis are isostructural with the binary MVO$_5$ (M = Nb, Ta) oxides. They are orthorhombic, space group P_{nma}, Z = 4, and the cell parameters are for x = 0.79; a = 11.8899(7) Å, b = 5.5294(4) Å, c = 6.9505(5) Å; for x = 0.53: a = 11.8916(9) Å, b = 5.5309(4) Å, c = 6.9502(6) Å; and for x = 0.26: a = 11.893(1) Å, b = 5.5327(6) Å, c = 6.9468(9) Å. All these materials can be considered as members of the structural family of the so-called "monophosphate tungsten bronzes," (MPTB), (PO$_2$)$_4$(WO$_3$)$_{2m}$, with a value of m = 2. The refinements of the atomic positions have been obtained by Rietveld's method. The Ta$_x$Nb$_{1-x}$VO$_5$ compounds constitute a solid solution in the studied composition range. XRD and ED indicate the random distribution of Nb and Ta in these ternary mixed oxides. © 1992 Academic Press, Inc.

Introduction

Recently (*1*), we have shown the possibility to synthesize "via" sol–gel mixed oxides of general formula MVO$_5$ (M = Nb, Ta). In particular, this method is appropriate for the synthesis of the NbVO$_5$ oxide which, at the moment, has not been synthesized by using another procedure. These mixed oxides are isostructural with the β-forms of MPO$_5$ (M = Nb, Ta) compounds (*2, 3*) and can be considered as belonging to the structural family of the so-called "monophosphate tungsten bronzes" (MPTB) (*4–8*) of general formula (PO$_2$)$_4$(WO$_3$)$_{2m}$, in this case m = 2. The MPTB compounds are widely studied by their particular structure in channels, which can be of interest in the field of the inclusion compounds as host lattice of metallic ions (*9*).

Taking into account the advantage that the "sol–gel" methods supposed in the synthesis of the binary MVO$_5$ (M = Nb, Ta) oxide (*1a*), as well as the isostructural character of both compounds, it has been considered of interest the extension of this synthesis process to the obtention of the new mixed oxides (ternary oxides) in the Ta–Nb–V–O system, as well as the study of the structural modifications associated to the substitution degree (Ta → Nb) in these compounds.

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                    ┌─────────┐
                    │   H₂O   │
                    │ (ⁱPrOH) │
                    └─────────┘
                         │ 1 st. addition
                         ▼
┌─────────┐          ┌─────────┐          ┌───────────┐
│  NbCl₅  │ 2 nd.    │  TaCl₅  │ 2 nd.    │ (ᵗBuO)₃VO │
│ (ⁱPrOH) │ addition │ (ⁱPrOH) │ addition │  (ⁱPrOH)  │
└─────────┘ ───────► └─────────┘ ◄─────── └───────────┘
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                    ┌─────────┐
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                         │ crystallization
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                ┌───────────────┐
                │ Taₓ Nb₍₁₋ₓ₎VO₅ │
                └───────────────┘
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SCHEME 1.

Experimental

Synthesis of $Ta_xNb_{1-x}VO_5$ (0 < x < 1)

Niobium pentachloride (Fluka 99.9%), tantalum pentachloride (Fluka 99.9%), and vanadyl tritertbutoxide (prepared as it is described in Ref. (10)) have been used as starting materials. Appropriate amounts of the reagents (Ta : Nb : V), to reach the x : (1 − x) : 1 (x = 0.26, 0.53, and 0.79) molar ratio, were carefully mixed under dry conditions (dry box, N_2 flux). In a first step (Scheme 1), a solution of water/isopropanol (1 : 20) was added with a rate of approximately 1 ml/min to a dilute solution (1 : 100 molar ratio in isopropanol) of tantalum pentachloride; afterwards, two solutions of niobium pentachloride and vanadyl tritertbutoxide in isopropanol were added simultaneously, with a 3 : 1 relative rate of addition, respectively. The resulting light-yellow solution (sol), was poured into Petri dishes inside a hermetically close container with an initially relative humidity of about 63%. Experiments were carried out in a thermostated room at 295 ± 1 K. Under these conditions the gelation time is reached between 10 and 12 hr. Afterwards, the gel (yellow) is allowed to dry in air, giving the corresponding mixed precursor xerogel (brown), which is then reduced to fine powder, washed until elimination of Cl^- ions, and, finally, thermally treated in air at 873 K for 6 hr in a platinum crucible.

Characterization

X-ray powder diffraction patterns were registered in reflection mode using a Philips model PW1010 instrument equipped with a Cu anode and Ni filter, working at a scanning rate of 0.5° (2Θ)/min for 5° < 2Θ < 60°. For structural studies one set of powder X-ray diffraction data were collected from

each of the samples with crystal monochro-
mated CuKα radiation ($\lambda K\alpha_1$ = 1.5405 Å
and $\lambda K\alpha_2$ = 1.5443 Å) and a Θ-2Θ diffracto-
meter operating in the step scan mode at
5 sec per 0.04° step. Structure refinements
were carried out from the X-ray (211 reflec-
tions) data by applying Rietveld's method
(11), using the DWY 3.2 program converted
to PC by J. Rodriguez-Carvajal (12). In-
teratomic distances were calculated with the
program PARST (13) from the final atomic
positions.

Infrared (IR) spectra were recorded from
KBr pellets on a Perkin–Elmer 580B
double-beam dispersive spectrophotometer
coupled to a PE M3500 data station. Ther-
mal analysis, thermogravimetric and differ-
ential thermal analysis (TGA and DTA, re-
spectively) were carried out in static air
using a Stanton 750 equipment. The samples
(40–50 mg) were heated from room tempera-
ture to 873 K at heating rate of 10°C/min.

Samples for energy dispersive X-ray anal-
ysis (EDAX) were dispersed in water, laid
on a cooper grid, and coated with carbon.
The data were obtained with an EDAX 9100
analyzer computer system, coupled to a
transmission electron microscopy (TEM)
Philips EM420 apparatus, employing the fol-
lowing conditions: accelerating voltage, 120
KV; mean count rate, 2000–4000 counts/
sec; take off angle, 50°; and X-ray counts
made over a counting time of 100 sec. The
analysis data have been carried out on iso-
lated particles of different cells of the grid.
The X-ray emission spectra were treated in
the following way: (1) subtraction of the grid
contribution, and (2) subtraction of continu-
ous X-ray background by nonlinear interpo-
lation routine. The quantitative composition
of the ternary oxides was determined by
chemical analysis from induced coupled
plasma (ICP; Perkin–Elmer, 2000) and cal-
culated by the site occupancy obtained from
Rietveld refinements.

The electron diffraction patterns were ob-
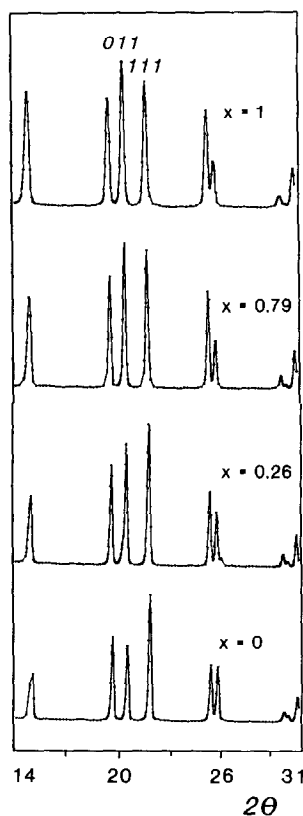tained by an electron microscope JEOL

FIG. 1. X-ray diffraction diagrams of the $Ta_xNb_{1-x}VO_5$
mixed oxides.

2000 FX; the accelerating potential was 200
KV. The samples were crushed in an agatha
mortar, dispersed in acetone, and then
mounted on carbon coated microgrids.

Results and Discussion

The study by X-ray diffraction of the sam-
ples, obtained as in the Experimental sec-
tion, shows that the thermal treatment of the
precursor xerogels at 873 K for 6 hr leads,
for all the compositions studied, to crystal-
line samples. In Fig. 1 we have compared
the XRD diagrams of the crystalline samples
in the $Ta_xNb_{1-x}VO_5$ system corresponding
to different compositions (x = 0.26, 0.79),
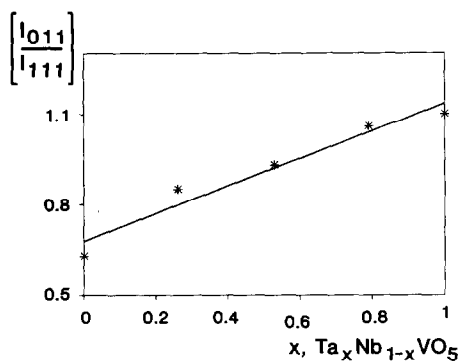with those of the binary MVO_5 (M = Nb,

FIG. 2. Relative intensity $[I_{011}/I_{111}]$ of the X-ray diffraction peaks vs the substitution degree, x, in the Ta$_x$Nb$_{1-x}$VO$_5$ mixed oxides.

TABLE I

STOICHIOMETRIC FORMULA DETERMINED BY (i) CHEMICAL ANALYSIS (ICP), (ii) REFINEMENT OF THE SITE OCCUPANCY FOR Nb AND Ta, USING RIETVELD'S METHOD, (iii) EDAX MICROPROBE

Sample	ICP	DRX (Rietveld)	EDAX
T79N21	Ta$_{.79}$Nb$_{.21}$VO$_5$	Ta$_{.78}$Nb$_{.22}$VO$_5$	Ta$_{.86}$Nb$_{.21}$V$_{.93}$O$_5$
T53N47	Ta$_{.53}$Nb$_{.47}$VO$_5$	Ta$_{.58}$Nb$_{.42}$VO$_5$	Ta$_{.49}$Nb$_{.50}$V$_{1.01}$O$_5$
T26N74	Ta$_{.26}$Nb$_{.74}$VO$_5$	Ta$_{.20}$Nb$_{.80}$VO$_5$	Ta$_{.35}$Nb$_{.74}$V$_{.91}$O$_5$

Ta) oxides $(1, 14)$. The intensity of the diffraction peaks in compounds of the Ta$_x$Nb$_{1-x}$VO$_5$ system is affected by the metallic substitution degree (x) (Fig. 2) in relation to the change of atomic number (Nb : 41; Ta : 73). The position of those peaks is, in general, very close to that of the binary oxides in agreement with the analogies between the ionic radius of Ta^{5+} (VI) and Nb^{5+} (VI) (15) as well as between their electronegativities (16). In this case, these similarities prevent a convenient characterization of the system by this technique, because it is not possible to distinguish between a pure ternary oxide and a mixture of binary oxides in the adequate molar relation.

To evaluate the obtention of a ternary oxide in this system, first we have used the technique of TEM-EDAX. As a general rule, it is observed for all the analyzed compositions, a good homogeneity in the distribution of the three elements (Ta, Nb, V). Table I shows the EDAX analysis data for different samples; the results obtained agree reasonably well with those estimated by other techniques (ICP, Rietveld's method). We have also compared the DTA curve of the amorphous xerogel precursor of the Ta$_{0.53}$Nb$_{0.47}$VO$_5$ oxide with those corresponding to the double MVO$_5$ (M = Nb, Ta)

oxides, respectively. As it is shown in Fig. 3, in the region from 673 to 873 K exothermic peaks are observed, which can be assigned to crystallization processes. The appearance of only a single peak for the sample of composition Ta$_{0.53}$Nb$_{0.47}$VO$_5$, at 756 K, which is not coincident with those observed neither for NbVO$_5$ or TaVO$_5$ binary oxides (707 and 839 K, respectively), corroborates the formation of a ternary oxide by heating of the corresponding precursor xerogel.

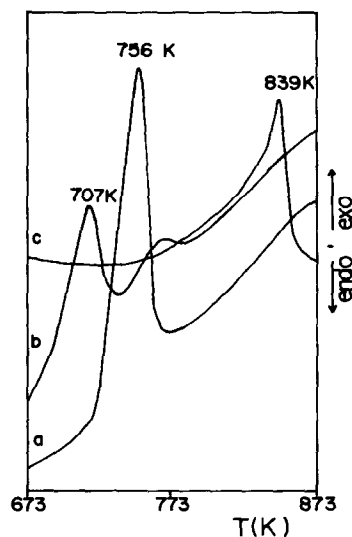All the above results show that the sol–gel procedure is an adequate method to synthe-

FIG. 3. Differential thermal analysis of the precursor xerogels of (a) Ta$_{0.53}$Nb$_{0.47}$VO$_5$, (b) NbVO$_5$, and (c) TaVO$_5$.
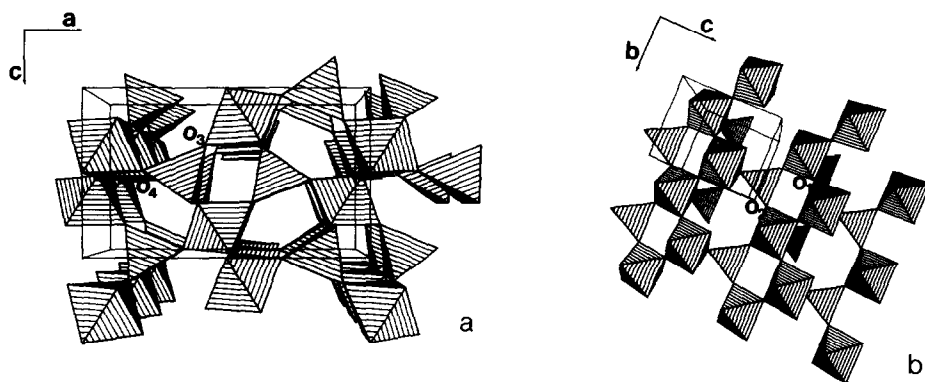
FIG. 4. Projection of the structure of $Ta_xNb_{1-x}VO_5$ mixed oxides on the (a) (010) plane and (b) (100) plane.

size ternary oxides in all the composition range of the studied system. This possibility to change Nb by Ta is in agreement with the extensive solubility observed for Ta_2O_5 in the different Nb_2O_5 allotropic forms described by Goldschmidt (17).

The XRD study of the $Ta_xNb_{1-x}VO_5$ materials shows that they are isostructural with the binary MVO_5 (M = Nb, Ta) oxides. The general structure of these compounds can be described by chains of $[MO_6]$ (M = Nb, Ta) octahedra along the [010] direction (Fig. 4b), arranged in zig-zag on the (010) plane and linked by $[VO_4]$ tetrahedra. Such an arrangement defines in the [010] direction two types of empty channels: larger of pentagonal section and smaller with rhomboidal section (Fig. 4a).

The refinements of the structural parameters were carried out using Rietveld's method. The initial model was the proposed by Chahboun et al. (14) for $TaVO_5$; we assumed here the statistical substitution of niobium by tantalum in octahedrical position based both on the electron diffraction of the samples, in which there are not indications of a regular distribution of the octahedral cations and, on the DRX diagrams, in which are not observed the existence of additional superstructure peaks. The site occupancy

factors for Nb^{5+} and Ta^{5+} ions were refined simultaneously under the constraint that all of the tantalum sites were occupied either by Ta^{5+} or by Nb^{5+} ions. The atomic position obtained after refinements for all the synthesized materials are summarized in Table II, as well as cell parameters, sites occupancy, and R factors. These results show a high analogy between cell parameters for $Ta_xNb_{1-x}VO_5$ ($0 < x < 1$) compounds with different compositions, in agreement with the similarity of the positions of the diffracton peaks in the corresponding XRD diagrams. In Table III are listed the interatomic distances for the $Ta_xNb_{1-x}VO_5$ oxides, the results obtained showing the distortion of coordination polyhedra both for the vanadium tetrahedra and for the niobium/tantalum octahedra. By using the empirical formula (18)

$$\%D = \frac{100}{d_a^2} \sum (d_i - d_a)^2 \qquad (1)$$

d_i = interatomic distance
d_a = average interatomic distance

we have compared the distortion degree and the average interatomic distances of the structural polyhedra of different compounds in which vanadium is located in tetrahedral coordination and/or niobium and tantalum

TABLE II

ATOMIC PARAMETERS FOR Ta$_x$Nb$_{1-x}$VO$_5$ OXIDES

	Cell Parameters		
Samples	a (Å)	b (Å)	c (Å)
T79N21[a]	11.8899(7)	5.5294(4)	6.9505(5)
T53N47[a]	11.8916(9)	5.5309(4)	6.9502(6)
T26N74[a]	11.893(1)	5.5327(6)	6.9468(9)

Atomic positions

	Nb				Ta			
	x	y	z	N	x	y	z	N
T79N21	.0592(4)	.25	.3442(7)	.113(4)	.0592(4)	.25	.3442(7)	.387(4)
T53N47	.0592(6)	.25	.345(1)	.210(4)	.0592(6)	.25	.345(1)	.290(4)
T26N74	.0590(6)	.25	.346(1)	.40(1)	.0590(6)	.25	.346(1)	.09(1)

	V				O(1)			
	x	y	z	N	x	y	z	N
T79N21	.343(1)	.25	.525(2)	.5	0	0	.5	.5
T53N47	.342(1)	.25	.524(2)	.5	0	0	.5	.5
T26N74	.343(1)	.25	.525(2)	.5	0	0	.5	.5

	O(2)				O(3)			
	x	y	z	N	x	y	z	N
T79N21	.131(2)	−.012(5)	.164(5)	1.0	.200(4)	.25	.470(6)	.5
T53N47	.129(2)	−.012(6)	.165(6)	1.0	.190(4)	.25	.463(7)	.5
T26N74	.127(2)	−.009(5)	.173(5)	1.0	.200(4)	.25	.470(6)	.5

	O(4)				R Factors			
	x	y	z	N	R_{WP}	R_{Bragg}	R_E	χ^2
T79N21	.420(4)	.25	.313(6)	5	14.36	11.03	4.6	9.7
T53N47	.425(4)	.25	.311(7)	5	16.78	12.44	4.4	14.5
T26N74	.418(4)	.25	.311(6)	5	20.19	12.88	5.0	16.4

Note.

$$R_{wp} = 100 \times \frac{\sum_i w_i [y_i(\text{obs}) - y_i(\text{cal})]^2}{\sum_i \sqrt{w_i * y_i(\text{obs})^2}}$$

$$R_{Bragg} = 100 \times \frac{\sum_k [I_k(\text{obs}) - I_k(\text{cal})]}{\sum_k I_k(\text{obs})}$$

$$R_E = 100 \times \sqrt{\frac{(N - P + C)}{\sum_i w_i y_i(\text{obs})^2}}$$

$$\chi^2 = \frac{R_{wp}^2}{R_E^2} = \frac{\sum_i w_i [y_i [y_i(\text{obs}) - y_i(\text{cal})]^2}{(N - P + C)},$$

where $(N - P + C)$ is the degrees of freedom.

[a] T79N21 is Ta$_{0.79}$Nb$_{0.21}$VO$_5$ oxide, T53N47 is Ta$_{0.53}$Nb$_{0.47}$VO$_5$ oxide, and T26N74 is Ta$_{0.26}$Nb$_{0.74}$VO$_5$ oxide.

TABLE III

INTERATOMIC DISTANCES CALCULATED FROM
RESULTS OF TABLE II

Distances (Å) [MO$_6$] Octahedral	Samples		
	T79N21	T53N47	T26N74
M–O(1) *2	1.892(3)	1.889(5)	1.884(5)
M–O(2) *2	2.10(3)	2.09(4)	2.04(3)
M–O(3) *1	1.89(5)	1.76(5)	1.88(5)
M–O(4) *1	1.98(5)	1.93(5)	2.00(5)
O(1)–O(1) *1	2.7647(2)	2.7655(2)	2.7664(3)
O(1)–O(2) *2	2.81(3)	2.79(4)	2.73(3)
O(1)–O(3) *2	2.76(4)	2.66(4)	2.76(4)
O(1)–O(4) *2	2.70(5)	2.72(4)	2.74(4)
O(2)–O(2) *1	2.90(4)	2.90(5)	2.86(4)
O(2)–O(3) *2	2.70(5)	2.63(5)	2.66(5)
O(2)–O(4) *2	2.90(5)	2.83(5)	2.87(5)
[VO$_4$] Tetrahedral			
V–O(2) *2	1.66(3)	1.68(3)	1.72(3)
V–O(3) *1	1.74(5)	1.86(5)	1.74(5)
V–O(4) *1	1.73(4)	1.78(5)	1.73(4)
O(2)–O(2) *1	2.63(4)	2.63(5)	2.67(4)
O(2)–O(3) *2	2.75(5)	2.89(5)	2.83(5)
O(2)–O(4) *2	2.84(5)	2.86(6)	2.90(5)
O(3)–O(4) *1	2.83(7)	2.99(7)	2.82(7)

are in octahedral coordination (Table IV). It is observed, that the values obtained for the ternary oxides are generally in the same order of magnitude that those obtained for related compounds.

In Fig. 5 it is shown the IR spectra (1250–250 cm^{-1}) of some Ta$_x$Nb$_{1-x}$VO$_5$ oxides (Fig. 5b); in part (a), we have represented for comparison those corresponding to NbVO$_5$ and TaVO$_5$ ($x = 0$ and 1, respectively) mixed oxides. As it was discussed elsewhere (1a), the most intense bands observed in this region are the stretching mode vibrations of M–O groups. Although it is difficult to assign all the bands in the IR spectrum of this region, especially due to the overlapping of the bands attributed to the V–O and Nb–O stretching vibrations, we have assigned tentatively the observed

bands by correlation with isostructural compounds (1, 14, 19), with data of IR spectra of orthovanadates (20), as well as by the evolution of the bands with the content in Nb or Ta in the ternary oxide. To try to define the position of the bands, especially in the case in which the overlapping of bands characteristic of V–O and Nb–O groups occurs, as the Ta$_{0.53}$Nb$_{0.47}$VO$_5$ oxide, the deconvolution of the M–O stretching bands into its components was carried out using a computer program based in that proposed by Pitha and Jones (21). The corresponding results are collected in Table V.

As it was observed in the IR spectra of the related MVO$_5$ (M = Nb, Ta) oxides (1, 14), all these spectra shown an intense band centered at 810 cm^{-1}, which can be attributed to ν_3 mode of vibration of [VO$_4$] species. In addition a shoulder, centered at 920 cm^{-1}, can be assigned to the ν_1 mode of the orthovanadate. The latter, which is IR forbidden in XY_4 groups in T_d symmetry, becomes active when a distortion of the tetrahedral groups occurs, due to the change of the characteristic symmetry (22, 23). Bands at about 730 and 670 cm^{-1} can be related to stretching vibration of Nb–O groups and Ta–O groups, respectively.
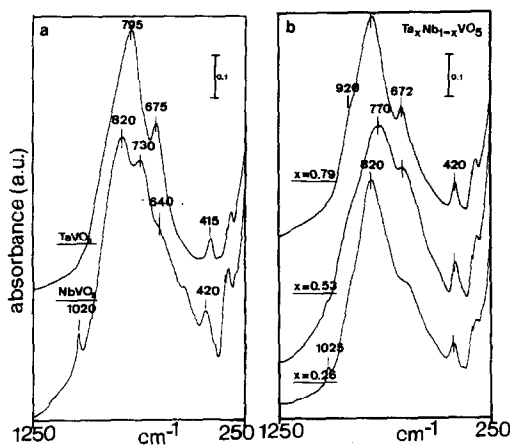

FIG. 5. IR spectra of (a) MVO$_5$ (M = Nb, Ta) oxides and (b) Ta$_x$Nb$_{1-x}$VO$_5$ compounds.

TABLE IV

DISTORTION DEGREE (%) OF THE STRUCTURAL POLYHEDRA AND AVERAGE INTERATOMIC
DISTANCE FOR $Ta_xNb_{1-x}VO_5$ MIXED OXIDES AND RELATED COMPOUNDS

Samples	Octahedral		Tetrahedral		Reference
	Distortion	$\langle M-O \rangle$	Distortion	$\langle M-O \rangle$	
$TaVO_5$	1.6	2.0(1)	0.13	1.67(3)	(14)
T79N21	1.4	2.0(1)	0.20	1.70(4)	This work
T53N47	2.6	1.9(1)	0.74	1.75(9)	This work
T26N74	0.8	1.95(8)	0.01	1.73(1)	This work
$NbVO_5$	0.8	1.92(8)	0.5	1.77(8)	(18, 24)
$BaNb_2V_2O_5$	0.9	1.96(8)	0.15	1.71(4)	(25)
	0.50	1.96(6)	—	—	
β-$NbPO_5$	0.53	1.96(6)			(3)
	0.6	1.97(4)	—	—	
β-$TaPO_5$	0.3	1.90(4)			(2)
$LiNbWO_6$	0.4	1.98(5)	—	—	(26)
	1.9	2.0(1)			
	2.0	2.0(1)	—	—	
$Na_4Nb_8P_6O_{35}$	0.5	2.07(6)			(27)
YVO_4	—	—	0.00	1.71	(28)
$InVO_4$	—	—	0.56	1.73(7)	(29)
			0.56	1.72(7)	
	—	—	0.43	1.73(6)	
$FeVO_4$			0.36	1.72(6)	(30)

Conclusion

Sol–gel appears as an appropriate method for the synthesis of xerogel precursors able to form crystalline ternary oxides in the Ta–Nb–V–O system, of general formula $Ta_xNb_{1-x}VO_5$. The XRD and ED studies show the existence of a solid solution between $NbVO_5$ and $TaVO_5$ in all range of composition and the random distribution of Nb and Ta in octahedral position. The presence of channels in the structure and the existence of elements able to change easily the oxidation state makes these materials interesting to act as potential host lattices for metal insertion processes.

TABLE V

ASSIGNMENT OF THE FREQUENCIES OBTAINED FROM DECONVOLUTION OF THE IR ABSORPTION BAND (M–O STRETCHING REGION) OF $Ta_xNb_{1-x}VO_5$ ($0 \leq x \leq 1$) MIXED OXIDES

$NbVO_5$	T26N74	T73N47	T79N21	$TaVO_5$	Assign.
903	903	920	910	883	ν (V–O)
815	815	813	806	795	
732	752	743	740	—	ν (Nb–O)
—	634	658	658	676	ν (Ta–O)

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