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Preparation and optical characteristics of novel oxynitride phases in the $R_3(\text{Ta/Nb})\text{-O-N}$ system ($R = \text{La, Eu, Gd, Ho, Y, Yb}$).

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Keywords

Rare earth tantalates/niobates, oxynitrides, optical properties, solid solution

Abstract

The synthesis of reactive nitridation precursors prepared by the citrate route has been evidenced with the $R_3\text{TaO}_7$ and $R_3\text{NbO}_7$ stoichiometries ($R = \text{La, Eu, Gd, Ho, Y, Yb}$). Novel oxynitride phases have been isolated in the fluorite-type series $R_3\text{Ta}(\text{O,N},\square)_8$ and $R_3\text{Nb}(\text{O,N},\square)_8$ where $\square$ represents anionic vacancies. The niobium/tantalum substitution leads to a modification of the absorption properties towards higher wavelengths. The comparison between GdT_a , Gd_2T_a and Gd_3T_a -based oxynitride phases highlights a blue shift of the position of the absorption edge with increasing Gd/Ta ratio. Unlike with RT_a and R_2T_a stoichiometries, R_3T_a - oxynitride phases generally show a very narrow formation range in temperatures as well as low absorption in the visible.

1. Introduction

Oxynitride phases belonging to the R-Ta-O-N system were recently studied with the RTa and R₂Ta stoichiometries [1-2]. Reactions between rare-earth tantalates RTaO₄ and ammonia flow at 950°C form oxynitrides with different structures depending on the size of the R element: perovskite RTaON₂, pyrochlore R₂Ta₂O₅N₂ (R = Nd to Gd) and defect fluorite RTa(O,N,□)₄ for R = [Ho, Er, Yb, Y] (□ represents an anionic vacancy) [1]. The RTa-O-N oxynitrides with fluorite structure form solid solution domains with variable nitrogen contents and related colors. The color of the YTa(O,N,□)₄ powders varies from yellow (after 15h nitridation) to brown for the most substituted compositions (after 90h). Fluorite-type phases have been also evidenced in the oxynitride series R₂Ta(O,N,□)₆ with R = [Nd to Yb, Y]. Gd₂Ta(O,N,□)₆ manifests a bright yellow hue characterized by the CIE color coordinates L = 95, a* = 2 and b* = 19 [2].

In the present study, we have pursued our investigations with the exploration of the R₃Ta stoichiometry. Our interest focused particularly on the gadolinium phase in order to compare its optical characteristics with the previously obtained results in the GdT₃O₇-O-N and Gd₂Ta-O-N stoichiometries [1, 2]. We have also studied the analog compositions by fully substituting niobium for tantalum atoms. Few papers have been devoted to the preparation of R₃TaO₇ and R₃NbO₇ ternary oxides. Reports on the crystal structure of R₃TaO₇ are often confused. Indeed, Yokogawa *et al.* have reported that R₃TaO₇ compounds showed several polymorphic modifications based on fluorite-related structures [3]. Generally, it is accepted that the decrease in the R³⁺ ionic radii leads to a crystal structure of higher symmetry characterized by disordered distributions of cations or anions. The crystal structure of the compounds shifts respectively from

orthorhombic weberite to pyrochlore, and then to defect fluorite from R = La to Yb [4, 5]. La_3TaO_7 and La_3NbO_7 samples prepared by a polymerized complex method are metastable and show a phase transition occurring around 1050 and 1000°C respectively, from cubic pyrochlore to orthorhombic weberite [6, 7]. Similar structure-types were evidenced with R_3NbO_7 compositions [8].

The incorporation of nitrogen within such oxide systems allows to shift the absorption edge towards visible wavelengths [9]. In particular, our attention focused on the effect of nitrogen on the colors resulting from the nitridation treatment. Nitride and oxynitride materials display interesting optical properties that can be developed, in a non-exhaustive reference list, among pigments, UV absorbers, visible-light-driven photocatalysts [9-13] or phosphors [14, 15]. Among them, nitrogen-doped TiO_2 is one of the most investigated material to degrade organic molecules in air or water under visible light [16, 17]. However, oxynitrides and nitrides, containing more nitrogen, exhibit promising performances for overall water splitting to produce hydrogen [18-20].

2. Experimental

2.1. Preparation

R_3TaO_7 tantalates and R_3NbO_7 niobates were prepared using the amorphous citrate route involving citric acid as a complexing agent. This calcination method of metal-organic complexes produces ultrafine reactive powders with an excellent chemical homogeneity [10]. Rare-earth oxides (Eu_2O_3 , Ho_2O_3 , Yb_2O_3) dissolved in concentrated hydrochloric acid (37%, Merck), rare-earth nitrates (for lanthanum, gadolinium, yttrium) dissolved in distilled water, niobium ammonium oxalate (H.C. Starck) and a tantalum oxalate solution (H.C. Starck) in water were used as starting

materials. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$, Merck, >99%.) dissolved in a minimum amount of water was added to each solution in the proportion of 1 mol per cation valence, the addition being followed by a 30 min stirring step at 120 °C. Since the complexation of cations by citric acid is improved at $\text{pH} \geq 7$, the acidic solutions were neutralized by ammonia solution (25%, Merck) [21]. Then the solutions were mixed together and stirred at 150 °C for 20 min to promote chelate formation. The liquid was progressively heated up to 250 °C, leading after 5 h to an expanded black solid residue. This solid was finally ground and calcined at 600 °C in air in an alumina crucible until elimination of carbon. X-ray amorphous powders are generally produced with a high reactivity for nitridation.

Nitridation reactions were carried out in alumina boats placed inside an electric furnace through which ammonia gas flowed with a flow rate of 20 L.h^{-1} . The temperature was raised between 700 and 950 °C at a heating rate of 10 $^{\circ}\text{C.min}^{-1}$. Generally, after a 15 h reaction time, the furnace was switched off and the nitrided powders were allowed to cool to room temperature under nitrogen atmosphere.

2.2. Characterization

XRD powder patterns were recorded using a Philips PW3710 diffractometer operating with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). X'PERT softwares – Data Collector and Graphics, and Identify – were used, respectively, for pattern recording, analysis and phase matching. The lattice parameters were refined using Dicvol04 [22].

Nitrogen and oxygen contents were determined with a LECO[®] TC-600 analyzer using the inert gas fusion method. Nitrogen was measured as N_2 by thermal conductivity and oxygen as CO_2 by infrared detection. The apparatus was calibrated using Leco[®]

standard oxides as well as ϵ -TaN as a nitrogen standard [23]. The estimation of the error on the measurement is lower than 5%.

Diffuse reflectance spectra were collected using a Varian Cary 100 Scan spectrometer equipped with the Varian WinUV software and the integrated sphere Labsphere (DRC-CA-30I). Prior to measurements, the absolute reflectance of the samples was calibrated with a certified "spectralon" standard (Labsphere Cie). Experimental data were collected within the 250-800 nm range with 1 nm step and 0.5 s integration time. The position of the absorption edge was determined graphically at the inflexion point of the curve and the value of the optical gap using the theory of Kubelka-Munk [24]. The CIE $L^*a^*b^*$ color coordinates, L: brightness axis, a^* : green to red axis, b^* : blue to yellow axis, were deduced from the diffuse reflectance spectra (Varian software: WinUV Color Application). Energy-dispersive Spectrometry (EDS) has been used to determine the R:(Ta,Nb) ratio of the samples. The EDS analysis system works as an integrated feature of a scanning electron microscope (JEOL JSM 6400).

3. Results and Discussion

3.1. R_3TaO_7 / R_3NbO_7 oxide precursors

Rare-earth tantalates and niobates form a large family of compositions with the stoichiometries $R(Ta/Nb)O_4$, $R_3(Ta/Nb)O_7$, $R(Ta/Nb)_3O_9$, $R(Ta/Nb)_7O_{19}$, $R_3(Ta/Nb)O_6$ [25]. In this work, our contribution to the system R-Ta-O-N is extended to the nitridation of the R_3TaO_7 compositions ($R = La, Eu, Gd, Ho, Y, Yb$). Among the possibilities offered by the complexation-calcination method, oxide precursors can be prepared as reactive X-ray amorphous powders. This route often allows to prepare

metastable oxides as reported in the $Y_6(W,Mo)O_{12}$ solid solution for which a cubic structure is observed at low temperatures instead of the thermodynamically stable rhombohedral one [26]. In the present study, the thermal reaction of amorphous precursors at 1000°C during 15h leads unambiguously to a crystallized fluorite-type phase R_3TaO_7 , as shown for gadolinium in Fig. 1a, except for the lanthanum compound that crystallizes in an orthorhombic weberite structure ($a = 11.118(7)$ Å, $b = 7.733(9)$ Å, $c = 7.582(4)$ Å, Cmc m) in agreement with the JCPDF file 38-1418 (Table 1). Such oxides can also be synthesized using a conventional ceramic route by heating a mixture of R_2O_3 and Ta_2O_5 (or Nb_2O_5) oxides at much higher temperatures ($> 1350^\circ\text{C}$) [3,4]. However, the interpretation of the crystal structure appears to be confusing between authors. In the diffraction pattern of Gd_3TaO_7 prepared by a polymerized complex method Abe et al. underlined the presence of several superlattice lines at 1350°C that prove the formation of a cubic pyrochlore structure, while Cai and Yokogawa indicate the formation of a weberite structure [3-8]. Under our experimental conditions using the citrate route and low temperatures, we have only observed the fluorite-type structure without any superlattice lines. The discrepancies about the R_3TaO_7 structures comes mainly from the preparation route or the reaction temperature. All the structures are related to the fluorite-type. The use of *chimie douce* routes involves often the formation of metastable phases, leading to a competition between such phases and thermodynamically stable structures. The corresponding formulas R_3TaO_7 and R_3NbO_7 were confirmed by EDS and Leco® analyses (Table 1 and 2). Experimental oxygen contents are in good agreement with the calculated values. For example, in the case of Gd_3TaO_7 , the experimental oxygen amount (14.9 ± 0.1 wt.%) matches well with the

calculated one (14.65 wt.%). All the samples are colorless except the holmium containing product for which the pale yellow results from 4f-4f transitions.

XRD patterns observed for R_3NbO_7 are close to those of R_3TaO_7 (Fig. 2a), evidencing a slight difference in the lattice parameters (Tables 1 and 2). R_3NbO_7 phases with $R = Eu, Gd, Ho, Y, Yb$ present a defect fluorite structure. The values of the cubic unit cell parameter decrease from europium to ytterbium and follow a linear relation. All R_3TaO_7 and R_3NbO_7 oxides were used in their X-ray amorphous state as precursors for nitridation. Similarly to the tantalum based compositions, R_3NbO_7 powders are colorless (except for holmium).

3.2. $R_3(Ta/Nb)(O,N,\square)_8$ oxynitrides

The characteristics of the nitrated phases are given in Tables 3 and 4 for Ta- and Nb-based samples. The thermal reaction of the R_3TaO_7 oxide precursors for the larger rare-earth elements $R = La$ and Eu leads to a mixture of La_2O_3 and $LaTaON_2$ perovskite and a mixture Eu_3TaO_7 (defect fluorite) + $EuTa(O,N)_3$ (perovskite) respectively. It has not been possible to prepare an oxynitride single phase for these elements which may be attributed to the size of the involved lanthanides. La^{3+} ions are too large to fit in the 8-fold coordinated sites available in the R_3TaO_7 fluorite-type structure and therefore occupy the 12-fold coordinated site in the perovskite structure. By comparison the case of Eu^{3+} is different. Eu^{3+} has a similar ionic radius than Gd^{3+} but under the reducing synthesis conditions, Eu^{3+} is reduced to Eu^{2+} which leads to the formation of the $EuTa(O,N)_3$ [27].

In the case of gadolinium, the X-ray diffraction pattern indicates the formation of a fluorite-type phase (Fig. 1b). Using the experimental nitrogen content (1.00 wt.%)

and the electroneutrality of the formula, we have calculated the resulting defect fluorite composition $\text{Gd}_3\text{TaO}_{5.67}\text{N}_{0.88}\square_{1.45}$ for the sample nitrated at 950°C during 15h (Table 3). A heating at higher temperature (1100°C) under NH_3 leads to a black mixture composed of the nitride phase, Ta_2O_5 and Gd_2O_3 (Fig. 1c). As indicated in Table 5, the corresponding position of the absorption edge is located in the UV range of the spectrum ($\lambda = 323$ nm, bandgap = 3.71 eV) resulting in a colorless powder (Fig. 3). Thus, the insertion of nitrogen in such a phase is not sufficient to generate an absorption in the visible. In order to shift the absorption edge towards larger wavelengths, we have totally substituted tantalum by niobium which has a higher electronegativity. It results a gadolinium-based oxynitride fluorite that is obtained at lower temperature (850°C) compared to the case of tantalum (Fig. 2b). A reaction over 900°C evidenced the formation of Nb(O,N) secondary phase (Fig. 2c). As expected, the ensuing diffuse reflectance study indicates an absorption edge shifted to 440 nm for $\text{Gd}_3\text{NbO}_{6.17}\text{N}_{0.56}\square_{1.27}$ (Fig. 3). The higher covalency of the Nb-based phase explains the larger shift of the absorption edge when nitrated, compared to the tantalum one. For isostructural compounds the band gap decreases as the effective electronegativity of the transition metal ion increases [28]. From the spectrum profile of $\text{Gd}_3\text{NbO}_{6.17}\text{N}_{0.56}\square_{1.27}$ are derived the color coordinates $L = 83$, $a^* = 1$, $b^* = 16$ that are typical of the observed pale yellow color. Corresponding Gd_3Nb - and Gd_3Ta -based oxynitride phases have close lattice parameters, in relation with similar Ta^{5+} and Nb^{5+} ionic radii in 6-fold (0.64 Å) and 8-fold (0.74 Å) coordinated sites [21]. We observe the possibility to prepare an oxynitride fluorite phase with europium at 700°C which was not possible under our conditions with the analog tantalum composition (Table 4).

The R/Ta ratio influences also the characteristics of the series $R_x\text{Ta-O-N}$. The phases prepared and listed in Table 5 present a fluorite symmetry, except for the ratio $\text{Gd/Ta}=1$ where an orange powder of the perovskite structure can be isolated at high temperature [1]. No evidence of low intensity extra peaks was pointed out as a sign of structural modification of the pyrochlore type for example. We observe increasing cubic parameters from the RTa to the R_3Ta oxynitride stoichiometries due to an increase of the radius of the average cation. When comparing the characteristics within the $\text{Gd}_x\text{Ta-O-N}$ series, a shift of the absorption edge towards UV is observed on the diffuse reflectance spectrum with increasing Gd/Ta ratio in parallel with a change in color from yellow to white (Fig. 4). The study has been extended in a similar approach to compositions with different Gd/Nb ratios in order to evaluate the effect of the substitution on the color. Unfortunately, the nitridation of the amorphous oxide GdNbO_4 prepared by the citrate route leads to a mixture $\text{Gd}_2\text{O}_3 + \text{Nb(O,N)}$. Although no oxide phase was reported with the stoichiometry $\text{Gd}_2\text{NbO}_{5.5}$, the ammonolysis of this amorphous phase between 700°C and 900°C produces a grey oxynitride powder with a fluorite structure, whereas at 1000°C , a mixture $\text{Gd}_2\text{O}_3 + \text{Nb(O,N)}$ is formed. These stoichiometries are thus not intended for suitable optical properties.

With the smaller rare earth elements $R = \text{Ho, Y, Yb}$, novel Ta and Nb-based oxynitride phases have been isolated with a defect fluorite structure (Tables 3 and 4). Corresponding lattice parameters follow a linear relation and decrease from gadolinium to ytterbium as expected (Fig. 5). Compared to the corresponding oxide precursors (Tables 1 and 2), Ta and Nb-based oxynitrides show higher parameter values due to the insertion of nitrogen (Tables 3 and 4). In the case of Yb, both tantalum-based oxide and

oxynitride parameters are very close. As indicated in Tables 3 and 4, the powders are generally little colored with a poor brightness. Similarly to the case of gadolinium, when modifying the ratio from RTa to R₂Ta and R₃Ta ratios, the oxynitride unit cell parameter increases, for example, respectively from 5.201(1) to 5.229(1) and 5.244(3) Å for Y and from 5.100(1) to 5.159(1) and 5.167(2) Å for Yb [1-2]. In comparison with RTa and R₂Ta samples, colored R₃Ta- and R₃Nb- oxynitrides manifest a limited thermal stability range of approximately 50°C around the reaction temperatures (T) given in Table 3 and 4. The increase of the reaction step to 3 cycles of 15 hours gives rise to a limited panel of nitrogen contents within the oxynitride compositions (Tables 6 and 7). The fluorite structure manifests enough flexibility in general to form domains of solid solutions, quite restricted in our case, at 950°C for Ta compositions and from 700 to 850°C for Nb samples. Compared to the ratio Gd/Ta = 1 [1], we observe with increasing nitridation time a decrease of the nitrogen content. We suppose that R₃Ta or R₃Nb-oxynitrides present a shorter range of stability compared to that of RTa or RNb compounds. A competition between nitrogen enrichment and decomposition may occur. Heatings performed over 950°C lead quite rapidly to dark powders, attesting of a partial reduction of the transition metal.

4. Conclusion

We have shown the possibility to insert nitrogen within R₃Ta-O and R₃Nb-O systems leading to fluorite-type oxynitrides. The panel of resulting colors do not lead to bright hues in comparison with previous work in the RTa stoichiometry. A blue shift of the absorption is clearly observed when increasing the R/Ta ratio. In order to modify the

colors of the oxynitrides, tantalum atoms were substituted by niobium atoms in the Gd_3TaO_7 precursor where a significant change of coloration is observed as a consequence of the shift of the absorption edge towards visible radiations. Solid solution domains obtained from $\text{R}=\text{Gd}$ to Yb in the R_3Ta and R_3Nb stoichiometries evidence a limited range of stability.

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Table 1Experimental characteristics of R_3TaO_7 phases prepared at 1000°C.

Element	XRD	Lattice parameters (Å)	O wt.% (experimental)	O wt.% (calculated)	Color
La	weberite	a = 11.118(7) b = 7.733(9) c = 7.582(4)	16.1	15.78	white
Eu	fluorite	5.319(3)	14.5	14.96	white
Gd	fluorite	5.307(3)	14.9	14.65	white
Ho	fluorite	5.223(4)	14.3	14.22	pale yellow
Y	fluorite	5.220(7)	19.9	20.01	white
Yb	fluorite	5.170(4)	14.1	13.79	white

Table 2Experimental characteristics of R_3NbO_7 phases prepared at 1000°C.

Element	XRD	Lattice parameter (Å)	O wt.% (experimental)	O wt.% (calculated)	color
Eu	fluorite	5.325(2)	16.7	16.95	white
Gd	fluorite	5.305(3)	16.4	16.55	white
Ho	fluorite	5.229(3)	16.3	16.01	pale yellow
Y	fluorite	5.241(2)	23.1	23.75	white
Yb	fluorite	5.191(2)	15.7	15.47	white

Table 3Experimental characteristics of nitrided R_3TaO_7 phases (950°C - 15h).

Element	XRD	Lattice parameter (Å)	N wt.% (experimental)	Formula	Color
La	$La_2O_3 + LaTaON_2$	-	-	-	orange
Eu	$Eu_3TaO_7 + EuTa(O,N)_3$	-	0.95	-	beige
Gd	defect fluorite	5.317(2)	1.64	$Gd_3TaO_{5.67}N_{0.88} \square_{1.45}$	white
Ho	defect fluorite	5.252(1)	1.32	$Ho_3TaO_{5.90}N_{0.73} \square_{1.37}$	pale yellow
Y	defect fluorite	5.244(3)	1.74	$Y_3TaO_{5.97}N_{0.69} \square_{1.34}$	whitish
Yb	defect fluorite	5.167(2)	1.62	$Yb_3TaO_{5.61}N_{0.93} \square_{1.46}$	beige

Table 4Experimental characteristics of nitrided of R_3NbO_7 phases (reaction step = 15h).

Element	XRD	Nitridation temperature (°C)	Lattice parameter (Å)	N wt.% (experimental)	Formula	Color
Eu	defect fluorite	700	5.331(2)	0.47	$Eu_3NbO_{6.67}N_{0.22}\square_{1.11}$	white
Gd	defect fluorite	850	5.316(2)	1.16	$Gd_3NbO_{6.17}N_{0.56}\square_{1.27}$	pale yellow
Ho	defect fluorite	700	5.248(2)	0.88	$Ho_3NbO_{6.34}N_{0.44}\square_{1.22}$	pale yellow
Y	defect fluorite	750	5.265(1)	1.88	$Y_3NbO_{6.06}N_{0.62}\square_{1.32}$	white
Yb	defect fluorite	700	5.194(1)	1.01	$Yb_3NbO_{6.22}N_{0.52}\square_{1.26}$	pale yellow

Table 5

Characteristic values from the diffuse reflectance spectra of the $\text{Gd}_x\text{Ta-O-N}$ samples series.

Composition	Gd/Ta	Lattice parameter (Å)	$\lambda \pm \Delta\lambda$ (nm)	E_g (eV)	color
$\text{GdTaO}_{2.33}\text{N}_{1.12}\square_{0.55}$	1	5.205(2)	553 ± 70	2.58	yellow
GdTaON_2	1	$a = 5.552(3)$ $b = 5.690(2)$ $c = 7.923(3)$	561 ± 31	2.21	orange
$\text{Gd}_{2.4}\text{Ta}_{1.6}\text{O}_{3.26}\text{N}_{2.89}\square_{1.85}$	1.5	5.246(2)	428 ± 65	2.75	pale yellow
$\text{Gd}_{2.67}\text{Ta}_{1.33}\text{O}_{5.53}\text{N}_{1.20}\square_{1.27}$	2	5.271(4)	389 ± 55	3.04	pale yellow
$\text{Gd}_{2.86}\text{Ta}_{1.14}\text{O}_{6.16}\text{N}_{0.65}\square_{1.19}$	2.5	5.298(3)	337 ± 27	3.61	whitish
$\text{Gd}_3\text{TaO}_{5.67}\text{N}_{0.88}\square_{1.45}$	3	5.317(2)	323 ± 26	3.71	whitish

Table 6

$R_3Ta(O,N,\square)_8$ fluorite-type solid solutions: composition and color.

R	Thermal ammonolysis conditions	N wt. %	Experimental formulation	Color
Gd	5 h, 950°C	1.81	$Gd_3TaO_{5.54}N_{0.98}\square_{1.48}$	white
	15 h, 950°C	1.64	$Gd_3TaO_{5.67}N_{0.88}\square_{1.45}$	
Ho	15h, 950°C	1.32	$Ho_3TaO_{5.90}N_{0.73}\square_{1.37}$	pale yellow
	2 x 15h, 950°C	1.27	$Ho_3TaO_{5.94}N_{0.71}\square_{1.35}$	
Y	15h, 950°C	1.74	$Y_3TaO_{5.97}N_{0.69}\square_{1.34}$	whitish
	3 x 15h, 950°C	1.63	$Y_3TaO_{6.03}N_{0.64}\square_{1.33}$	
Yb	15h, 950°C	1.62	$Yb_3TaO_{5.61}N_{0.93}\square_{1.46}$	beige
	2 x 15h, 950°C	1.53	$Yb_3TaO_{5.68}N_{0.88}\square_{1.44}$	

Table 7

$R_3Nb(O,N,\square)_8$ fluorite-type solid solutions: composition and color.

R	Thermal ammonolysis	N wt. %	Experimental formulation	Color
Eu	15h, 700°C	0.47	$Eu_3NbO_{6.67}N_{0.22}\square_{1.11}$	white
	3 x 15h, 700°C	0.44	$Eu_3NbO_{6.69}N_{0.21}\square_{1.10}$	
Gd	15h, 850°C	1.16	$Gd_3NbO_{6.17}N_{0.56}\square_{1.27}$	pale yellow
	2 x 15h, 850°C	1.23	$Gd_3NbO_{6.12}N_{0.59}\square_{1.29}$	
Ho	15h, 700°C	0.88	$Ho_3NbO_{6.34}N_{0.44}\square_{1.22}$	pale yellow
	3 x 15h, 700°C	0.86	$Ho_3NbO_{6.36}N_{0.43}\square_{1.21}$	
Y	15h, 750°C	1.88	$Y_3NbO_{6.06}N_{0.62}\square_{1.32}$	white
	2 x 15h, 750°C	1.77	$Y_3NbO_{6.12}N_{0.59}\square_{1.29}$	
Yb	15h, 700°C	1.01	$Yb_3NbO_{6.22}N_{0.52}\square_{1.26}$	pale yellow
	3 x 15h, 700°C	0.87	$Yb_3NbO_{6.33}N_{0.45}\square_{1.22}$

Fig. 1. XRD powder pattern of Gd_3TaO_7 prepared at 1000°C (a), Gd_3TaO_7 nitrided at $950^\circ\text{C}/15\text{h}$ (b) corresponding to $\text{Gd}_3\text{TaO}_{5.67}\text{N}_{0.88}\text{O}_{1.45}$ and Gd_3TaO_7 nitrided at $1100^\circ\text{C}/15\text{h}$ (c) leading to a mixture including Gd_2O_3 (•) and Ta_2O_5 (+).

Fig. 2. XRD powder pattern of Gd_3NbO_7 prepared at 1000°C (a), Gd_3NbO_7 nitrided at 850°C/15h (b) and Gd_3NbO_7 nitrided at 900°C/15h (c) with the formation of $\text{Nb}(\text{O},\text{N})$ (+).

Fig 3. Diffuse reflectance spectra of the oxides Gd_3TaO_7 (a), Gd_3NbO_7 (b) and the corresponding oxynitrides $\text{Gd}_3\text{TaO}_{5.67}\text{N}_{0.88}\square_{1.45}$ (c) and $\text{Gd}_3\text{NbO}_{6.17}\text{N}_{0.56}\square_{1.27}$ (d).

Fig 4. Diffuse reflectance spectra of the oxynitrides: $\text{GdTaO}_{2.33}\text{N}_{1.12}\square_{0.55}$ (a), $\text{Gd}_{2.4}\text{Ta}_{1.6}\text{O}_{3.26}\text{N}_{2.89}\square_{1.85}$ (b), $\text{Gd}_{2.67}\text{Ta}_{1.33}\text{O}_{5.53}\text{N}_{1.20}\square_{1.27}$ (c), $\text{Gd}_{2.86}\text{Ta}_{1.14}\text{O}_{6.16}\text{N}_{0.65}\square_{1.19}$ (d), $\text{Gd}_3\text{TaO}_{5.67}\text{N}_{0.88}\square_{1.45}$ (e).

Fig. 5. Evolution of the lattice parameter with the rare-earth ionic radius in the tantalum (a) and niobium(b) cases.