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SYNTHESIS AND STRUCTURE OF NEW RARE EARTH TANTALATES $RE_xTa_2O_{5+1.5x}$ (RE= Eu, Yb).

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Abstract

At a pressure of 7.0 GPa and temperature 1100 C new europium and ytterbium tantalates were synthesized. Low hydrated amorphous tantalum, europium and ytterbium hydroxides were used as starting materials. It is shown that tantalates are crystallized in the structure type of F-Ta_2O_5..RE atoms replace water molecules in the channels of the structure, and tantalum in his positions do not substitute. As well aqueous as anhydrous compounds were obtained. The concentration of Eu and Yb is small and corresponds to the formula $Eu_{0.101}Ta_2O_{5.151}$ and $Yb_{0.067}Ta_2O_{5.1}$. It was found that even such a small amounts of rare-earth cations strongly compress the unit cell of F-Ta_2O_5.

Key words: *high pressure-high temperature treatment, tantalum pentoxide, low hydrated amorphous tantalum, europium and ytterbium hydroxides, rare-earth tantalates.*

1. INTRODUCTION

Hydrate F-Ta_2O_5*2/3H_2O and derived from it F-Ta_2O_5 oxide were obtained by thermobaric treatment of low hydrated amorphous tantalum hydroxide (Nikishina E.E. et all., 2002, Zibrov I.P. et all, 2003).

The structure of both compounds is built up from puckering planes of pentagonal bipyramids (PB) [TaO7], linked to each other by the columns of bisdisphenoids (BDP) [TaO8]. The large channels are limited by two planes of PB and two columns of BDP (Fig.5). In the initial hydrate channels are occupied by water molecules. After water removal at ambient pressure, the channels are reduced in size (collapse) and anhydrous oxide F-Ta_2O_5 is formed. The size of channels, as well as the distance between them is almost exactly the same as the same parameters in hexagonal tungsten bronzes (HTB) (Magnéli A., 1953, Filonenko V.P. et all, 2002, Grenthe C. et all, 2002). In (Zibrov I.P. et all, 2003) we have suggested the possibility of substitution of water molecules in the channels of the hydrate structure by metal atoms with the formation of oxidized compounds $Me_xTa_2O_{5+y}$, or bronze $Me_xTa_2O_5$.

In the first stage we have attempted to synthesize the oxidized phases in order to continue to move to the synthesis of a new class of compounds of tantalum bronzes. Rare earth elements were selected as metals which allow to trace the changes in structural parameters, depending on the cations size. This paper presents the results obtained using europium and ytterbium (Eu^{+3}, r = 1.21 Å (C.N. 8), Yb^{+3}, r = 1.12 Å (C.N. 8) (Shannon R.D. and Prewitt C.T., 1969)). Thus, the goal of this work was an attempt to replace the water molecules in the channels of the structure of F-Ta_2O_5*2/3H_2O by rare-earth atoms and determining the influence of these atoms on the structural parameters.

2. EXPERIMENTAL

Low hydrated amorphous tantalum hydroxide was prepared by interaction of solid tantalum pentachloride with ammonia solution by using known method (Nikishina E.E. et all., 2006). Low hydrated amorphous europium and ytterbium hydroxides were prepared by a similar way - the interaction of rare earth chlorides with ammonia solution (Korovin S.S., 1999). The content of oxides in the hydroxides obtained was determined using thermogravimetric analysis. Their content was: Ta_2O_5 - 82,3%, Eu_2O_3 - 76,7%, Yb_2O_3 - 72,0%.

For further synthesis of oxide phases, powder mixtures containing the calculated amount of the starting low hydrated amorphous hydroxides in relation 1:7 (in terms of oxide molar composition $RE_2O_3 \bullet 7Ta_2O_5$) were prepared . The hydroxide mixtures were stirred in water at 60 C for 4 hours using vibration followed by evaporation to remove water excess . The resulting powder was subjected to microwave treatment for 1.5 hours at W = 100 watts. The amount of water in the final material was 10-25%.

Method of material thermobaric treatment is described in detail in (Zibrov I.P. et all 1998, Filonenko V.P. and Zibrov I.P., 2001). Starting amorphous powder was pressed into pellets with a diameter of 5 mm and a height of 3 ÷4 mm. To prevent the chemical interaction samples were isolated from the graphite heater by the foil (Ta, W). P-T conditions of treatment corresponded to the stability range of F-Ta_2O_5 * 2/3H_2O on the phase diagram, namely, P = 6.0-8.0 GPa, T = 950-1150 C.

Extracted from the high pressure chamber samples were purified mechanically from the protective foil and subjected to X-ray phase analysis on a diffractometer AXS with the XY position-sensitive detector (Bruker, Germany). Selected for structural analysis samples were run in the Guinier-camera G670 (Huber, Germany) (Cu $K\alpha_1$ radiation).The obtained X-ray data were subjected to full-profile analysis procedure using the software package GSAS (Larson A.C. and Von Dreele R.B., 1987, Toby B. H., 2001). Differential thermal analysis (DTA) combined with thermogravimetry (TG) were carried out in air at the ULVAC TGD 7000 (Sinku-Riko, Japan).

3. RESULTS

The first experiments show that after P-T treatment samples contained 10-20% of foreign phases, which are not always able to identify. Moreover, the refinement of the compounds structure, in particular, occupancy of the positions in the channels show that the concentration of rare-earth atoms is much less of their content in the initial mixture. Therefore, for further work starting mixtures were diluted by half. For this purpose, to the material, consisting of 1mole fraction of RE_2O_3 and 7 mole fractions of Ta_2O_5, was added low hydrated amorphous tantalum hydroxide powder in an amount to provide a molar ratio of 1mole fraction of RE_2O_3 and 14 mole fractions of Ta_2O_5. The powders were thoroughly mixed first with the use of dry mix, and then under acetone.

In (2) noted that the stoichiometry of the F-phase unit cell is $Me_{12}O_{32}$, and required stoichiometry $Me_{12}O_{30}$ (Me_2O_5) is realized by two oxygen atoms deficiency on the cell, i.e. partial occupancy of the positions O(1) and O(3). Thus, the oxygen introduced into the cell by the rare earth atoms (about one atom O) may occupy positions O(1) and O(3). During structure refinement occupancy of the sites O(1) and O(3) was considered equal to 1.0, as slight deviations from this value had no effect on the parameters of refinement (the electron density associated with a less than one atom of oxygen in the cell is negligible compared to the electron density associated with the other atoms). Also, as in the case of pure F-Ta_2O_5, in compounds with rare earths anhydrous phases are crystallized significantly worse than the water phases, as evidenced by the width of the diffraction peaks of FWHM (Tables 1,4). Probably, this fact led to the emergence of strong correlations between site occupancy of the rare

earth in the channel of the structure and its thermal parameters, making it difficult to refine the position occupancy. Therefore, during the refinement of the structure of anhydrous phases the occupancy of rare earth atoms were fixed, and the value corresponded to site occupancy in the aqueous material. This step is completely justified, because removing water from compound can not change rare earth content in it. In refinement tested whether RE atoms substitute Ta in BDP or PB. It turned out that the RE atoms replace only the water, and tantalum is not (probably because of the large difference in the size of Ta and RE).

3.1. Eu

Thermogravimetric analysis of the sample with Eu after P-T treatment show (Fig.1) that the water is removed from the material in the range T ≈400-650 C, and the total amount is 1.1%. The breaking on the TG curve is associated with a strong exothermic effect at T = 550-600 C.

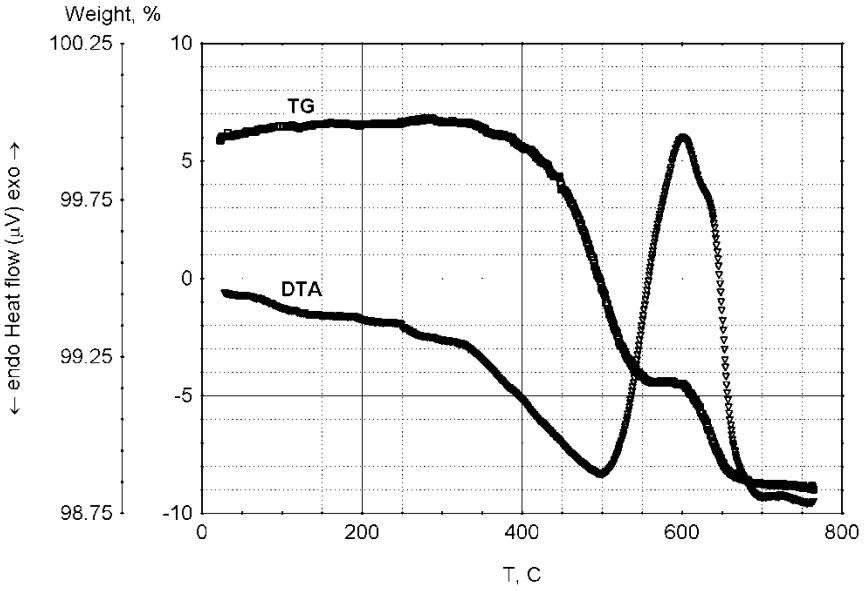
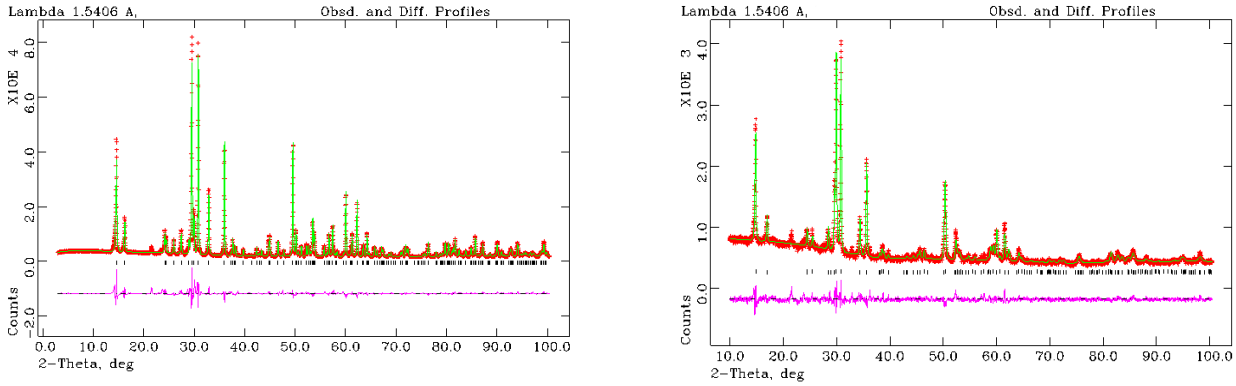


Fig.1. Thermogravimetric analysis of the sample $Eu_{0.101}Ta_2O_{5.151}*0.28H_2O$.

Sample weight - 45.7 mg, heating rate on air – 10 C/min.

Since at fully occupied positions in the channels water amount is 2.65% (which follows from the formulae $Ta_2O_5*2/3H_2O$), then the site occupancy of water in the channels is 1.1/2.65 =0.415. When conducting full-profile analysis this value was fixed and not refined. The structure of the phase is preserved upon heating in air up to T = 650 C. Thus, the anhydrous material was obtained whose structural parameters are also refined. The results of full-profile analysis for compounds $Eu_{0.101}Ta_2O_{5.151}*0.28H_2O$ and $Eu_{0.101}Ta_2O_{5.151}$ are shown on Fig.2 and presented in Table 1. Atomic coordinates, site occupancy and isotropic thermal parameters for these compounds are presented in Table 2 and selected interatomic distances - in Table 3.



a b

Fig.2. Rietveld refinement of $Eu_{0.101}Ta_2O_{5.151}$*0.28H_2O (a) и $Eu_{0.101}Ta_2O_{5.151}$ (b).

Observed (+), calculated (solid line)and the difference between observed and calculated (bottom curve) X-ray powder diffraction profiles are shown. The positions of all the allowed Bragg reflections are indicated by the row of vertical tick marks.

Table 1. Experimental detailes for $Eu_{0.101}Ta_2O_{5.151}$*0.28H_2O and $Eu_{0.101}Ta_2O_{5.151}$.

Chemical formula	$Eu_{0.101}Ta_2O_{5.151}$*0.28H_2O	$Eu_{0.101}Ta_2O_{5.151}$
Chemical formula weight	466.91	462.52
Space group	**I b a m**	**I b a m**
a (Å)	10.8809(1)	10.4177(2)
b (Å)	7.2678(1)	7.2681(1)
c (Å)	6.8489(1)	6.9831(1)
V (Å^3)	541.61(1)	528.74(1)
Z	6	6
D_x (Mg m^{-3})	8.589	8.716
R_F	0.043	0.098
R_P	0.061	0.037
R_{WP}	0.088	0.049
d (Durbin-Watson) (Hill R.J. and Flack H.D., 1987)	0.064	0.399
$FWHM_{min}$(°)	0.17	0.22
$FWHM_{max}$(°)	0.25	0.47
No of parameters used	49	47

Table 2. Fractional atomic coordinates, site occupancy and isotropic displacement parameters U_{iso} ($Å^2$) for $Eu_{0.101}Ta_2O_{5.151}$*0.28H_2O and $Eu_{0.101}Ta_2O_{5.151}$.

Atom	***Site***	***OCC***	*x*	*y*	*z*	U_{iso}
$Eu_{0.101}Ta_2O_{5.151}$*0.28H_2O						
Ta1	8(j)	1.0	0.2296(1)	0.2317(1)	0	0.0105(3)
Ta2	4(a)	1.0	0	0	0.25	0.0114(4)
O1	16(k)	1.0	0.1501(6)	0.1896(10)	0.2881(10)	0.0201(25)
O2	8(j)	1.0	0.1909(9)	0.5076(15)	0	0.0180(32)
O3	8(j)	1.0	0.0577(9)	0.1279(13)	0	0.0260(40)
Eu	4(b)	0.151(3)	0	0.5	0.25	0.0637(42)
H_2O	4(b)	0.415	0	0.5	0.25	0.0637(42)
$Eu_{0.101}Ta_2O_{5.151}$						
Ta1	8(j)	1.0	0.2351(2)	0.2533(6)	0	0.0645(10)
Ta2	4(a)	1.0	0	0	0.25	0.0085(7)
O1	16(k)	1.0	0.1363(7)	0.1847(14)	0.2834(25)	0.0866(63)
O2	8(j)	1.0	0.1414(11)	0.5505 (28)	0	0.0280(65)
O3	8(j)	1.0	0.0910(16)	0.1117(25)	0	0.163(13)
Eu	4(b)	0.151	0	0.5	0.25	-0.054(3)

Table 3. Selected interatomic distances r_{ij} (Å) for $Eu_{0.101}Ta_2O_{5.151}$*0.28$H_2O$and $Eu_{0.101}Ta_2O_{5.151}$.

	r_{ij} ($Eu_{0.101}Ta_2O_{5.151}$*0.28H_2O)	r_{ij} ($Eu_{0.101}Ta_2O_{5.151}$)
Ta1-O1	2.176(7) x2	2.286(15) x2
Ta1-O1	2.037(7) x2	2.070(14) x2
Ta1-O2	2.049(11)	2.370(20)
Ta1-O2	1.844(11)	1.957(19)
Ta1-O3	2.017(10)	1.821(15)
Ta2-O1	2.153(6) x4	1.968(9) x4
Ta2-O3	2.047(5) x4	2.146(9) x4
Eu-O1	2.797(7)x4	2.706(10)x4
Eu-O2	2.693(7)x4	2.314(8)x4
O1-O1	2.402(15)	2.594(15)
O1-O3	2.259(14)	2.103(17)
O3-O3	2.243(16)	2.496(15)

3.2. Yb

Thermogravimetric analysis of the sample with ytterbium after P-T treatment show (Fig.3) that the water starts to move away from the material already at 200 C and ends at 500-600 C. The total amount is 1.2%. The breaking on the TG curve at T = 550-600 C is associated with a strong exothermic effect .

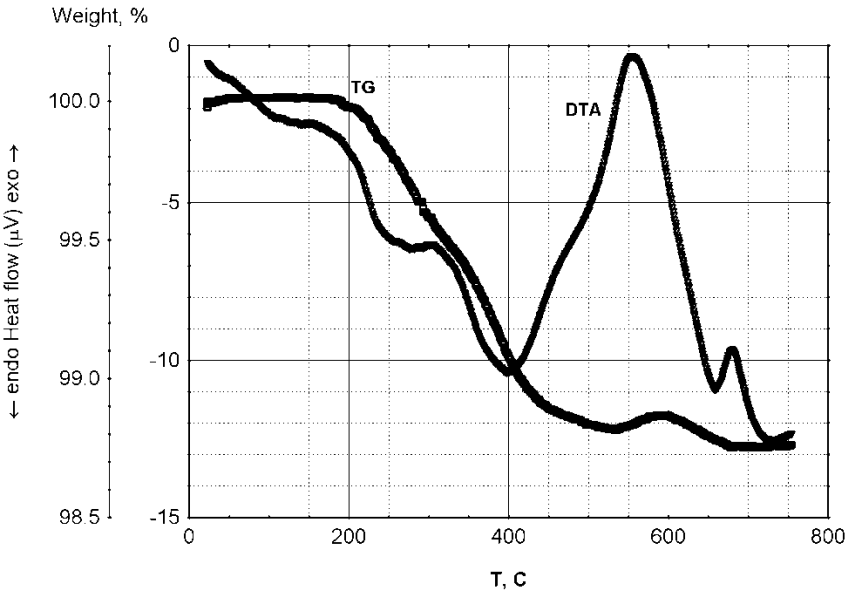
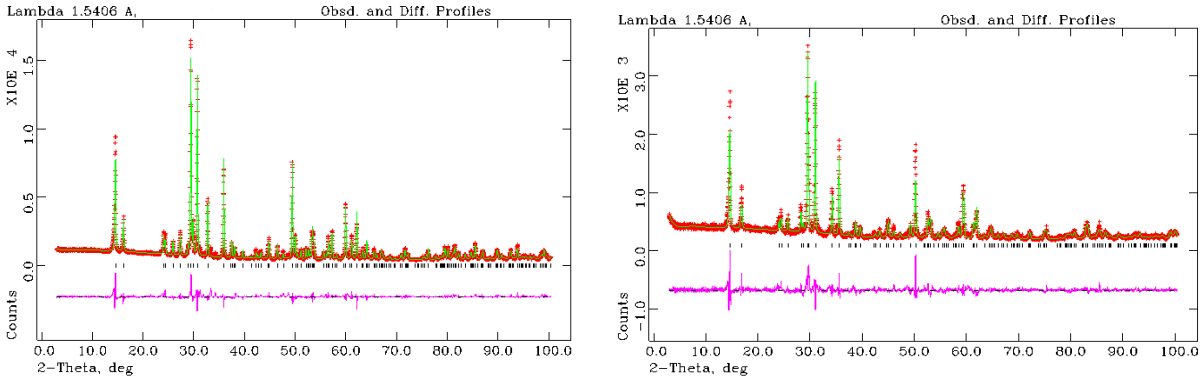


Fig.3. Thermogravimetric analysis of the sample $Yb_{0.067}Ta_2O_{5.1}$*$0.3H_2O$.
Sample weight - 52.2 mg, heating rate on air – 10 C/min.

Occupancy of water positions in the channels of the structure is as follows: 1.2/2.65 =0.45. When conducting full-profile analysis this value was fixed and not refined. The structure of the phase is preserved upon heating in air up to T =650 C. Thus, the anhydrous material was obtained whose structural parameters are also refined. The results of full-profile analysis for compounds $Yb_{0.067}Ta_2O_{5.1}$*$0.3H_2O$ and $Yb_{0.067}Ta_2O_{5.1}$ are shown in Fig.4 and presented in Table 4. Atomic coordinates, site occupancy and isotropic thermal parameters for these compounds are presented in Table 5 and selected interatomic distances - in Table 6.



a b

Fig.4. Rietveld refinement of $Yb_{0.067}Ta_2O_{5.1}$*$0.3H_2O$ (a) and $Yb_{0.067}Ta_2O_{5.1}$ (b).

Observed (+), calculated (solid line)and the difference between observed and calculated (bottom curve) X-ray powder diffraction profiles are shown. The positions of all the allowed Bragg reflections are indicated by the row of vertical tick marks.

Table 4. Experimental detailes for $Yb_{0.067}Ta_2O_{5.1}$*$0.3H_2O$ and $Yb_{0.067}Ta_2O_{5.1}$.

Chemical formula	$Yb_{0.067}Ta_2O_{5.1}$*$0.3H_2O$	$Yb_{0.067}Ta_2O_{5.1}$
Chemical formula weight	463.53	458.76
Space group	**I b a m**	**I b a m**
a (Å)	10.9071(1)	10.4546(2)
b (Å)	7.2761(1)	7.3845(2)
c (Å)	6.8562(1)	6.8916(1)
V ($Å^3$)	544.12(1)	532.05(1)
Z	6	6
D_x (Mg m^{-3})	8.488	8.591
R_F	0.060	0.107
R_P	0.062	0.065
R_{WP}	0.084	0.087
d (Durbin-Watson) (Hill R.J. and Flack H.D., 1987)	0.085	0.25
$FWHM_{min}$(°)	0.18	0.18
$FWHM_{max}$(°)	0.25	0.64
No of parameters used	45	43

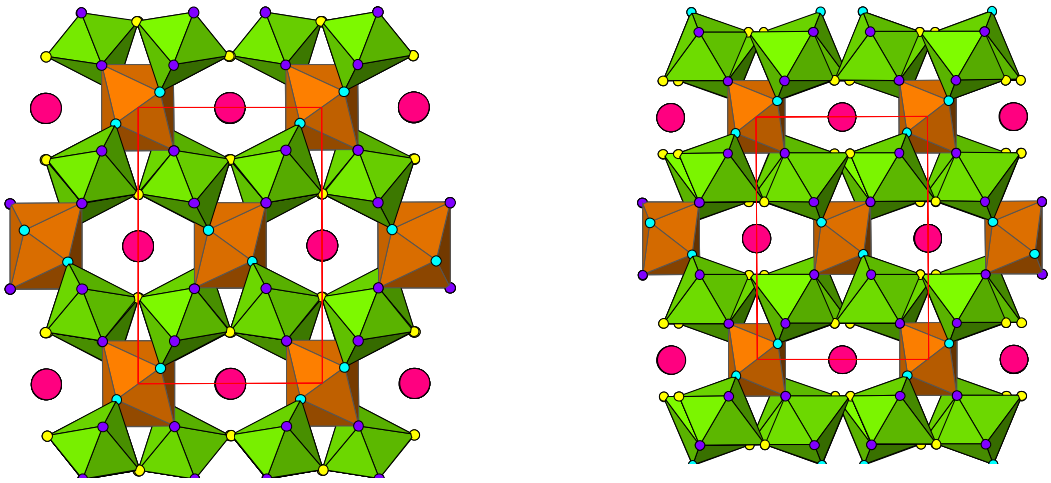
Table 5. Fractional atomic coordinates, site occupancy and isotropic displacement parameters U_{iso} ($Å^2$) for $Yb_{0.067}Ta_2O_{5.1}$*0.3H_2O and $Yb_{0.067}Ta_2O_{5.1}$.

Atom	***Site***	***OCC***	*x*	*y*	*z*	U_{iso}
$Yb_{0.067}Ta_2O_{5.1}$*0.3H_2O						
Ta1	8(j)	1.0	0.2294(1)	0.2329(1)	0	0.0133(3)
Ta2	4(a)	1.0	0	0	0.25	0.0166(4)
O1	16(k)	1.0	0.1547(5)	0.1955(8)	0.2910(8)	0.0087(19)
O2	8(j)	1.0	0.1874(8)	0.4968(15)	0	0.0347(31)
O3	8(j)	1.0	0.0573(7)	0.1192(11)	0	0.0162(31)
Yb	4(b)	0.100(2)	0	0.5	0.25	0.0973(50)
H_2O	4(b)	0.45	0	0.5	0.25	0.0973(50)
$Yb_{0.067}Ta_2O_{5.1}$						
Ta1	8(j)	1.0	0.2338(1)	0.2396(3)	0	0.0323(6)
Ta2	4(a)	1.0	0	0	0.25	0.0250(7)
O1	16(k)	1.0	0.1494(7)	0.1664(11)	0.2755(18)	0.0199(37)
O2	8(j)	1.0	0.1488(14)	0.4555(31)	0	0.0560(73)
O3	8(j)	1.0	0.0661(18)	0.1235(21)	0	0.0950(91)
Yb	4(b)	0.100	0	0.5	0.25	0.656(73)

Table 6. Selected interatomic distances r_{ij} (Å) for $Yb_{0.067}Ta_2O_{5.1}$*0.3H_2O and $Yb_{0.067}Ta_2O_{5.1}$.

	r_{ij} ($Yb_{0.067}Ta_2O_{5.1}$*0.3H_2O)	r_{ij} ($Yb_{0.067}Ta_2O_{5.1}$)
Ta1-O1	2.172(5) x2	2.163(11) x2
Ta1-O1	1.980(5) x2	2.091(10) x2
Ta1-O2	1.974(11)	2.422(21)
Ta1-O2	1.943(10)	1.816(21)
Ta1-O3	2.051(7)	1.955(17)
Ta2-O1	2.225(5) x4	1.993(7) x4
Ta2-O3	2.020(4) x4	2.064(9) x4
Yb-O1	2.799(6) x4	2.924(8) x4
Yb-O2	2.668(6) x4	2.356(10) x4
O1-O1	2.295(14)	2.467(15)

O1-O2	2.641(16)	
O1-O2	2.682(16)	
O1-O3	2.328(14)	2.114(15)
O3-O3	2.138(15)	2.274(16)



a b

Fig.5. The structure of $Yb_{0.067}Ta_2O_{5.1}$*0.3H_2O (a) и $Yb_{0.067}Ta_2O_{5.1}$ (b) along axis [001].
RE atoms and water molecules are shown as filled red circles. PB are green, BDP are brown.
This figure was drawn with the help of ATOMS program (Dowty E., 1989).

4. DISCUSSION

As shown above, the RE atoms substitute for water molecules in the studied structure. At the same time for greater Eu concentration is higher ($Me_{0.101}Ta_2O_{5.151}$) and for small Yb below ($Me_{0.067}Ta_2O_{5.1}$). X-ray data do not allow to do conclusions about the degree of uniformity of metal atoms distribution in the channels. This requires investigation by high resolution electron microscopy (HRTEM). Heating in air up to T = 600-650 C and the removal of water does not lead to the destruction of the cell, but only to its restructuring (a collapse of the channels), although the structure of the anhydrous compounds is strongly distorted. This process is accompanied by a strong exothermal effect (Fig.1,3). It is seen from Table 7 that a strongly charged cations RE^{+3} compress the cell so that its volume is significantly reduced compared to pure Ta_2O_5, most of anhydrous phases. Even larger europium compresses the cell stronger, because its concentration is higher than that of ytterbium. Heating in vacuum up to T = 450-500 C also leads to the removal of water without destroying of the cell. It should be noted that the structure of both aqueous and anhydrous phases contains very short (2.1-2.2 Å) O-O distances (Tables 3,6, (2)), which is unusual. This is probably a reflection of the fact that the material was synthesized under extreme conditions of high pressures and temperatures.

Table 7. Unit cell parameters (Å) and volume V (Å^3) of investigated compounds.

Compound	a	b	c	V
F-Ta_2O_5*2/3H_2O	10.9039(2)	7.2774(1)	6.8529(1)	543.79(1)
$Eu_{0.101}Ta_2O_{5.151}$*0.28H_2O	10.8809(1)	7.2678(1)	6.8489(1)	541.61(1)
$Yb_{0.067}Ta_2O_{5.1}$*0.3H_2O	10.9071(1)	7.2761(1)	6.8562(1)	544.12(1)
F-Ta_2O_5	10.4546(3)	7.3485(2)	6.9576(2)	534.52(2)
$Eu_{0.101}Ta_2O_{5.151}$	10.4177(2)	7.2681(1)	6.9831(1)	528.74(1)
$Yb_{0.067}Ta_2O_{5.1}$	10.4546(2)	7.3845(2)	6.8916(1)	532.05(1)

5. CONCLUSIONS

The experiments show that the RE atoms substitute for water molecules in the studied structure. The water also remains in the channels and occupies approximately 40% of positions. Metal atoms do not replace the tantalum in the BDP and the PB, but the water in the channels. Strongly charged cations RE^{+3} compress the unit cell so that its volume is significantly reduced compared to pure Ta_2O_5, most of anhydrous phases.

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