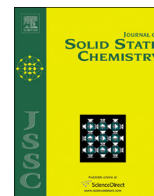




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journal homepage: www.elsevier.com/locate/jsscNew high pressure rare earth tantalates $RE_xTa_2O_{5+1.5x}$ ($RE = La, Eu, Yb$)Igor P. Zibrov^{a,*}, Vladimir P. Filonenko^a, Nikolai D. Zakharov^b, Peter Werner^b, Dmitrii V. Drobot^c, Elena E. Nikishina^c, Elena N. Lebedeva^c^a Institute for High Pressure Physics, Russian Academy of Sciences, Kaluzhskoe Highway 14, Troitsk, Moscow 142190, Russia^b Max Planck Institute for Microstructure Physics, Weinberg 2, D-06120 Halle/Saale, Germany^c Lomonosov Moscow University of Fine Chemical Technology, Prospect Vernadskogo 86, Moscow 119571, Russia

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ABSTRACT

Rare earth tantalates $La_{0.075}Ta_2O_{5.113}$, $Eu_{0.089}Ta_2O_{5.134}$ and $Yb_{0.051}Ta_2O_{5.077}$ have been prepared by solid state reaction at $P=7.0$ GPa and $T=1050$ – 1100 °C and studied by X-ray diffraction, thermal analysis and electron microscopy. Low hydrated amorphous tantalum, lanthanum, europium and ytterbium hydroxides were used as starting materials. Aqueous as well as anhydrous compounds were obtained. Title tantalates are crystallized in the structure type of $F-Ta_2O_5$ [Zibrov et al. Russ. J. Inorg. Chem. 48 (2003) 464–471] [5]. The structure was refined by the Rietveld method from X-ray powder diffractometer data: $La_{0.075}Ta_2O_{5.113}$, $a=10.5099(2)$, $b=7.2679(1)$, $c=6.9765(1)$ Å, $V=532.90(1)$ Å³, $Z=6$, space group $Ibam$; $Eu_{0.089}Ta_2O_{5.134}$, $a=10.4182(3)$, $b=7.2685(1)$, $c=6.9832(1)$ Å, $V=528.80(2)$ Å³, $Z=6$, space group $Ibam$; $Yb_{0.051}Ta_2O_{5.077}$, $a=10.4557(2)$, $b=7.3853(1)$, $c=6.8923(1)$ Å, $V=532.21(1)$ Å³, $Z=6$, space group $Ibam$. RE atoms do not replace the tantalum in its positions but the only water in the channels of the structure. Highly charged cations RE^{+3} compress the unit cell so that its volume becomes less than that of $F-Ta_2O_5$. Significant decrease of the unit cell volume after water removal from the structure is possible due to the puckering of pentagonal bipyramid layers and change of the corrugation angle in the layer.

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1. Introduction

Many of the tantalates are related to materials of electronics and optics because of their piezoelectrical, pyroelectrical, electro-optical, luminescent properties. In particular, geptatantalates $Eu_xLa_{1-x}Ta_7O_{19}$ and others are promising in terms of their luminescent properties [1–3]. So, searching for new tantalum oxides is very important for science and new technologies. Hydrate $F-Ta_2O_5 \cdot 2/3H_2O$ and derived from it $F-Ta_2O_5$ oxide were obtained by thermobaric treatment of low hydrated amorphous tantalum hydroxide [4,5]. The structure of both compounds is built up from puckering planes of pentagonal bipyramids (PB) [TaO_7], linked to each other by the columns of bisdisphenoids (BDP) [TaO_8]. The large channels are separated by two planes of PB and two columns of BDP (Fig. 1) and occupied by water molecules in the initial hydrate. 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 are almost exactly the same as the identical parameters in hexagonal

tungsten bronzes (HTB) [6–8]. We have suggested [5] 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 bronzes $Me_xTa_2O_5$.

In the first stage we have attempted to synthesize the oxidized phases. Rare earth elements were selected as metals which allow us to trace the evolution of structural parameters, as a function of the cations size. This paper presents the results obtained using large lanthanum (La^{+3} , $r=1.32$ Å (C.N. 8) [9]) middle europium (Eu^{+3} , $r=1.21$ Å (C.N. 8) [9]) and small ytterbium cations (Yb^{+3} , $r=1.12$ Å (C.N. 8) [9]). Thus, the goal of this work is to replace the water molecules in the channels of the $F-Ta_2O_5 \cdot 2/3H_2O$ structure by rare-earth atoms and to reveal the influence of these atoms on the structural parameters as well.

2. Experimental

Low hydrated amorphous tantalum hydroxide was prepared by interaction of solid tantalum pentachloride with ammonia solution by known method [4,10]. Low hydrated amorphous lanthanum, europium and ytterbium hydroxides were prepared by a similar way—the interaction of rare earth chlorides with ammonia solution [11,12]. For further synthesis of oxide phases, powder mixtures containing the calculated amount of the starting low hydrated amorphous hydroxides in relation 1:7 which corresponds to the

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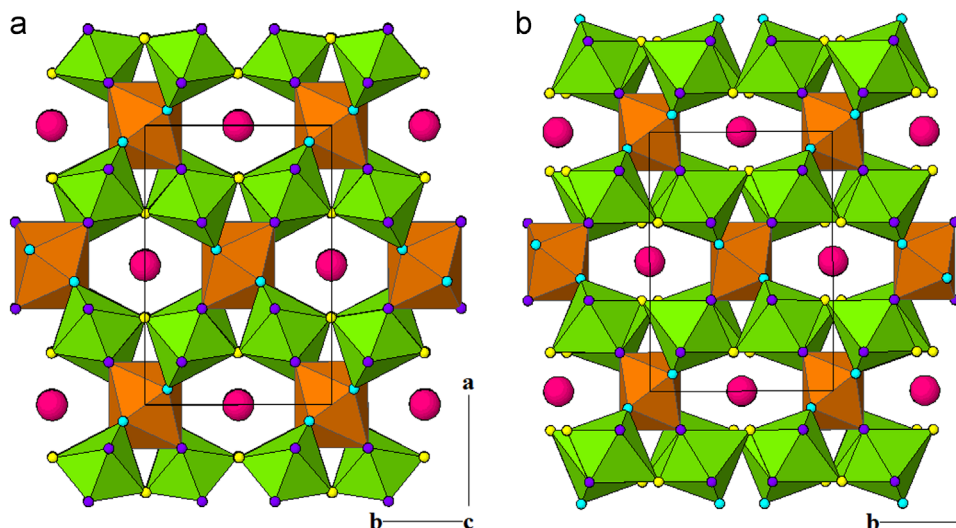


Fig. 1. The structure of $\text{Yb}_{0.051}\text{Ta}_2\text{O}_{5.077}\cdot 0.3\text{H}_2\text{O}$ (a) and $\text{Yb}_{0.051}\text{Ta}_2\text{O}_{5.077}$ (b) along axis [001]. RE atoms and water molecules are shown as red circles. Pentagonal bipyramids (PB) [TaO_7] are green, bisdisphenoids (BDP) [TaO_8] are brown. This figure was drawn with the help of ATOMS program [20]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

geptatantalates $\text{RETa}_7\text{O}_{19}$ composition (in terms of oxide molar composition $\text{RE}_2\text{O}_3\cdot 7\text{Ta}_2\text{O}_5$) were prepared. The hydroxide mixtures were stirred in water at 60 °C for 4 h using vibration followed by evaporation to remove water excess. The resulting powder was subjected to microwave treatment for 1.5 h at $W=100$ W. The amount of water in the final material was 10–25%.

Method of material thermobaric treatment is described in detail in [13,14]. 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). Synthesis was carried out at $P=7.0$ GPa, $T=1050\text{--}1100$ °C, $t=5$ min., i.e. in the stability range of $\text{F-Ta}_2\text{O}_5\cdot 2/3\text{H}_2\text{O}$ on the phase diagram, namely, $P=6.0\text{--}8.0$ GPa, $T=950\text{--}1150$ °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 Imaging Plate Guinier-camera G670 (Huber, Germany) ($\text{Cu } K\alpha_1$ radiation). The obtained X-ray data were subjected to full-profile analysis procedure using the software package GSAS [15,16]. The peak shapes could be described by a symmetric, or nearly symmetric, pseudo-Voigt function.

Differential thermal analysis (DTA) combined with thermogravimetry (TG) were carried out in air at the ULVAC TGD 7000 (Sinku-Riko, Japan).

IR absorption spectra were obtained on Fourier-spectrometer Vertex-70 (Bruker, Germany) in transmission mode with a resolution of 4 cm^{-1} . Pellets for experiments were pressed from mixture of pure KBr and 0.5% of the investigated material.

Specimens for High Resolution Transmission Electron Microscopy (HRTEM) investigations were prepared by crushing of small amount of the sample in an agate mortar with following dispersing it in butanol. Droplet of the suspension was put onto holey carbon film supported by a Cu grid. The microscope JEM4010 equipped with side entry goniometer and operated at 400 kV accelerating voltage was used. HRTEM images were taken at Scherzer underfocus $\Delta f=-30$ nm. At this defocus cation appear as a dark spots in the image [17]. The 200 kV electron microscope Philips CM20 equipped with high-angle side entry goniometer (maximum tilting angle $\pm 45^\circ$) and Energy Dispersive X-ray (EDX) detector was used to collect structural and compositional information as well from the same crystal fragment.

Table 1

Crystal data and structure refinement for $\text{Eu}_{0.089}\text{Ta}_2\text{O}_{5.134}\cdot 0.28\text{H}_2\text{O}$ and $\text{Eu}_{0.089}\text{Ta}_2\text{O}_{5.134}$.

	$\text{Eu}_{0.089}\text{Ta}_2\text{O}_{5.134}\cdot 0.28\text{H}_2\text{O}$	$\text{Eu}_{0.089}\text{Ta}_2\text{O}_{5.134}$
Chemical formula	$\text{Eu}_{0.089}\text{Ta}_2\text{O}_{5.134}\cdot 0.28\text{H}_2\text{O}$	$\text{Eu}_{0.089}\text{Ta}_2\text{O}_{5.134}$
Chemical formula weight	465.25	460.82
Space group	I b a m	I b a m
<i>a</i> (Å)	10.8812(1)	10.4182(3)
<i>b</i> (Å)	7.2681(1)	7.2685(1)
<i>c</i> (Å)	6.8492(1)	6.9832(1)
<i>V</i> (Å ³)	541.68(1)	528.80(2)
<i>Z</i>	6	6
<i>D_x</i> (Mg m ⁻³)	8.558	8.682
<i>R_F</i>	0.033	0.107
<i>R_P</i>	0.062	0.039
<i>R_{wp}</i>	0.088	0.041
<i>d</i> (Durbin–Watson [18])	0.062	0.355
FWHM _{min} (deg)	0.17	0.22
FWHM _{max} (deg)	0.25	0.47
No. of parameters used	51	46

Table 2

Crystal data and structure refinement for $\text{La}_{0.075}\text{Ta}_2\text{O}_{5.113}\cdot 0.47\text{H}_2\text{O}$ and $\text{La}_{0.075}\text{Ta}_2\text{O}_{5.113}$.

	$\text{La}_{0.075}\text{Ta}_2\text{O}_{5.113}\cdot 0.47\text{H}_2\text{O}$	$\text{La}_{0.075}\text{Ta}_2\text{O}_{5.113}$
Chemical formula	$\text{La}_{0.075}\text{Ta}_2\text{O}_{5.113}\cdot 0.47\text{H}_2\text{O}$	$\text{La}_{0.075}\text{Ta}_2\text{O}_{5.113}$
Chemical formula weight	465.17	457.69
Space group	I b a m	I b a m
<i>a</i> (Å)	10.8729(1)	10.5099(2)
<i>b</i> (Å)	7.2611(1)	7.2679(1)
<i>c</i> (Å)	6.8401(1)	6.9765(1)
<i>V</i> (Å ³)	540.02(1)	532.90(1)
<i>Z</i>	6	6
<i>D_x</i> (Mg m ⁻³)	8.582	8.557
<i>R_F</i>	0.039	0.074
<i>R_P</i>	0.062	0.065
<i>R_{wp}</i>	0.087	0.093
<i>d</i> (Durbin–Watson [18])	0.192	0.103
FWHM _{min} (deg)	0.09	0.09
FWHM _{max} (deg)	0.29	0.49
No. of parameters used	51	52

The first experiments show that after P–T treatment samples contained 10–20% of foreign phases, which are hard to identify. Moreover, the refinement of the compounds structure, in particular, occupancy of the positions in the channels show that the

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