

## Mechanochemical Synthesis of Tantalates of Rare-Earth Metals

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### Abstract

The investigation of phase composition in  $Y_2O_3 - Ta_2O_5$  and  $La_2O_3 - Ta_2O_5$  systems is carried out at mechanical activation and subsequent heat treatment. In  $Y_2O_3 - Ta_2O_5$  system the interaction of components is observed during mechanical activation. Heating of mechanically activated intermixtures of oxides leads to the formation of orthotantalates of yttrium and lanthanum. Temperature and time of complete interaction of components is much less than in a traditional ceramic method. The new convenient method of synthesis of tantalates of rare-earth metals is developed.

### INTRODUCTION

The tantalates of rare earths (RE) and solid solutions on their basis find application as materials for luminescent valves of high and low pressure, for coats of X-ray screens, are used as X-ray contrast substances for diagnostics of diseases [1–3].

The RE tantalates can be obtained by various methods. At solid phase synthesis from initial oxides, samples are carefully immixed in a stoichiometric ratio, molded and calcinated at temperature 1470–1620 K for 70 h with an intermediate grinding after 35 h. In another method of synthesis the initial oxides are mixed with flux and calcinated at 1270–1470 K for 24–30 h with intermediate homogenization of the mixture. Besides, the RE tantalates are obtained by hot pressing in vacuo of initial oxides at pressure 5.0–7.7 GPa, temperature 1770–1870 K for 5–10 min [1].

The known methods of preparation of tantalates have two essential deficiencies: the necessity of high temperatures and long time of synthesis. This leads to essential consumption of energy and rise in price of materials. Both deficiencies are caused by low reactivity of oxides participating in reaction, and

low rate of diffusion of components. Therefore, an increase of reactivity could promote decrease of energy, consumption for synthesis.

One of the most effective methods of increasing the reactivity is mechanochemical activation. As a rule, MCA results in the increase of diffusion rates. This served as the grounds to apply the MCA to the synthesis of rare earth tantalates. According to numerous literature data, one should expect the decrease of the interaction temperature and decrease of synthesis time resulting from the use of MCA. The synthesis of tantalates directly in mill drums could not be excluded.

The major goal of the present study is to demonstrate the possibility to use MCA for the synthesis the orthotantalates of yttrium ( $YTaO_4$ ) and tantalum ( $LaTaO_4$ ), which are promising X-ray contrast preparations for the diagnostics of some diseases.

### EXPERIMENTAL

The oxides of a tantalum ( $Ta_2O_5$ ), yttrium ( $Y_2O_3$ ), and lanthanum ( $La_2O_3$ ) were used for synthesis.

Mechanochemical activation of mixtures of oxides taken in the stoichiometrical ratios, carried out in a planetary centrifugal mill AGO-2 in barrels made of stainless steel by steel balls with a diameter of 5 mm at barrels rotation frequency of  $10 \text{ s}^{-1}$ . 5 g of amixture of oxides and 200 g of balls was loaded into a barrel; the barrels during activation were cooled by flowing water.

Thermograms were obtained with Q-1500D thermograf at heating rate of 1 deg/min, mass of sample being 200 mg. Diffraction patterns were obtained with a HZG-4C diffractometer with  $\text{CuK}_\alpha$  radiation and graphite monochromator on a diffracted beam. The diffraction patterns were recorded by scanning in points in an interval of angles  $2\theta = 10\text{--}75^\circ$ , step of scanning 0.050, time of scanning in a point being 3 s. The identification of the obtained diffraction patterns was made with a PC-PDF database. The unit cell parameters for  $\text{Y}_3\text{TaO}_7$  phase were determined on four most strong lines with the further refining by the least squares method.

## RESULTS AND DISCUSSION

### $\text{Y}_2\text{O}_3 - \text{Ta}_2\text{O}_5$ system

In the heat pattern of mechanically activated  $\text{Y}_2\text{O}_3\text{--Ta}_2\text{O}_5$  mixture, three exothermic

peak are observed with temperatures of maximums 1110, 1180, and 1260 K. Samples of mechanically activated mixture were calcined at these temperatures within 2 h and studied by X-ray diffraction.

An interaction of yttrium and tantalum oxides was observed already during MCA. The maximums allowing to identify the obtained phase as  $\text{Y}_3\text{TaO}_7$  are observed in X-ray diffraction patterns of the sample after MCA (Fig. 1). The observed maxima have low intensity and large half-widths, which means high dispersity and irregularity of crystalline structure. This is quite natural for this method of synthesis. According to the database, the  $\text{Y}_3\text{TaO}_7$  phase has cubic structure and unit cell parameter 10.5182 Å relating to  $Fd3m$  (227). However, unit cell parameter determined by us, using diffraction patterns is considerably diminished and has a value of  $(10.3692 \pm 0.0122)$  Å.

The diminished unit cell parameter points to the formation of a solid solution of replacement in the system. Molar ratio of oxides  $\text{Y}_2\text{O}_3/\text{Ta}_2\text{O}_5$  in activated mixture is 1 : 1, whereas in the observed phase this ratio is 3 : 1; thus, tantalum oxide appears is excess. As the ionic radius of  $\text{Ta}^{5+}$  is less than the ionic radius of  $\text{Y}^{3+}$ , the formation of a solid solution of

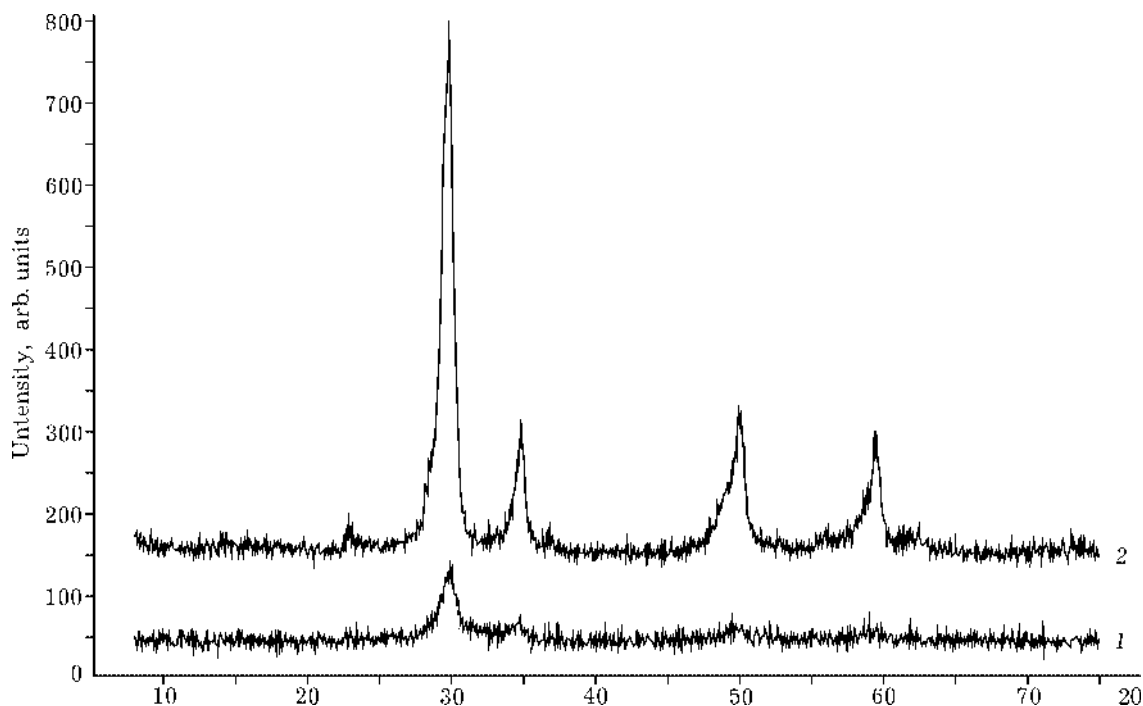


Fig. 1. Diffraction patterns of  $\text{Y}_2\text{O}_3 - \text{Ta}_2\text{O}_5$  sample after MCA (1) and subsequent calcination at 1110 K (2).

replacement leads to the decrease unit cell parameter. Oxidation degrees of yttrium and tantalum differ from each other; because of this, some changes of the crystal structure are necessary for the conservation of electrical neutrality. These changes are most likely to be oxygen vacancies ordered in one manner or another. Determination of detailed structure of the formed solid solution is the subject of a separate investigation and requires additional experimental data.

The calcination of mechanically activated sample at a temperature of 1110 K leads to the improvement of structure, which is expressed in the increase of intensity of diffraction peaks and decrease of their half-widths (see Fig. 1). At the same time, there is a further decrease of lattice constant down to  $(10.2942 \pm 0.0045)$  Å. This can be explained as follows: MCA causes the formation of solid solution based on  $Y_3TaO_7$ , and amorphisation of a part of tantalum oxide, which interacts at heat treatment with  $Y_3TaO_7$  phase and forms a solid solution with higher content of tantalum and smaller of a unit cell parameter.

After calcination at 1190 K, a mixture of two phases (Fig. 2) is observed in the sample: small amount of  $Y_3TaO_7$  and  $YTaO_4$  (card 12-1425, PC-PDF database). Lattice parameter for  $Y_3TaO_7$  phase comes closer to the reference

value. (An estimation of unit cell parameter for this sample was carried out using the only line 2.2.2. that is not superimposed with the lines of yttrium orthotantalate). This is the evidence of the decomposition of solid solution and participation of the released tantalum oxide in formation of yttrium orthotantalate phase of. Calcination of the sample at 1270 K leads to final formation of  $YTaO_4$  phase, since only a maxima related only to this phase are present in the diffraction patterns (see Fig 2).

### $La_2O_3 - Ta_2O_5$ system

Heat pattern of the sample of mechanically activated  $La_2O_3 - Ta_2O_5$  mixture contains only one exothermic peak with a maximum at 1180 K. The samples of mechanically activated mixture were annealed at 1100, 1180 and 1270 K for 2 h and studied by means of X-ray phase analysis.

After mechanical activation of  $La_2O_3 - Ta_2O_5$  mixture, the diffraction patterns of the sample (Fig. 3) contains maxima, corresponding to  $d-Ta_2O_5$  phase (card 12-1425, PC-PDF database). Maxima related to lanthanum oxide, are not observed. This fact can testify to amorphisation of lanthanum oxide as a result of MCA.

Heating up to temperatures below 1180 K does not lead to any appreciable changes dif-

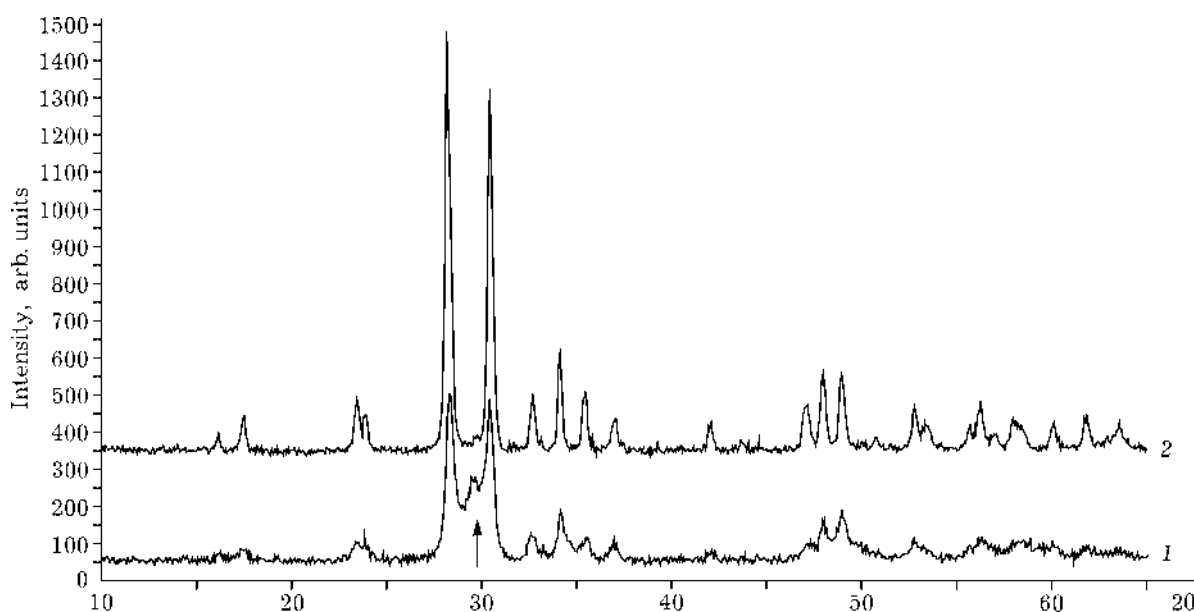


Fig. 2. Diffraction patterns of mechanically activated  $Y_2O_3 - Ta_2O_5$  sample after calcination at 1190 (1) and 1270 K (2). - reflection related to the  $Y_3TaO_7$  phase.

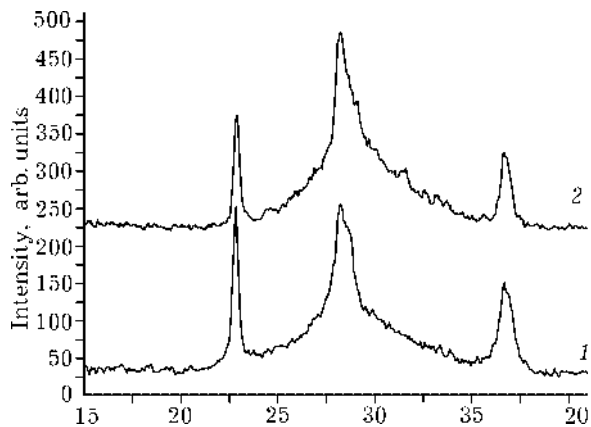


Fig. 3. Diffraction patterns of  $\text{La}_2\text{O}_3 - \text{Ta}_2\text{O}_5$  sample after MCA (1) and subsequent calcination at 1100 K (2).

fraction patterns (see Fig. 3). It is rather unusual fact, as one could expect at least crystallization of an amorphous phase of lanthanum oxide. At 1180 K, the formation of a phase of a trimetric tantalate of lanthanum  $\text{LaTaO}_4$  occurs. The observed set of diffraction peaks does not allow one to attribute them to any phase from PC-PDF database. The identification of the phase was made by comparison of the experimental patterns with theoretical ones, obtained with the structural data published in [4] (Fig. 4).

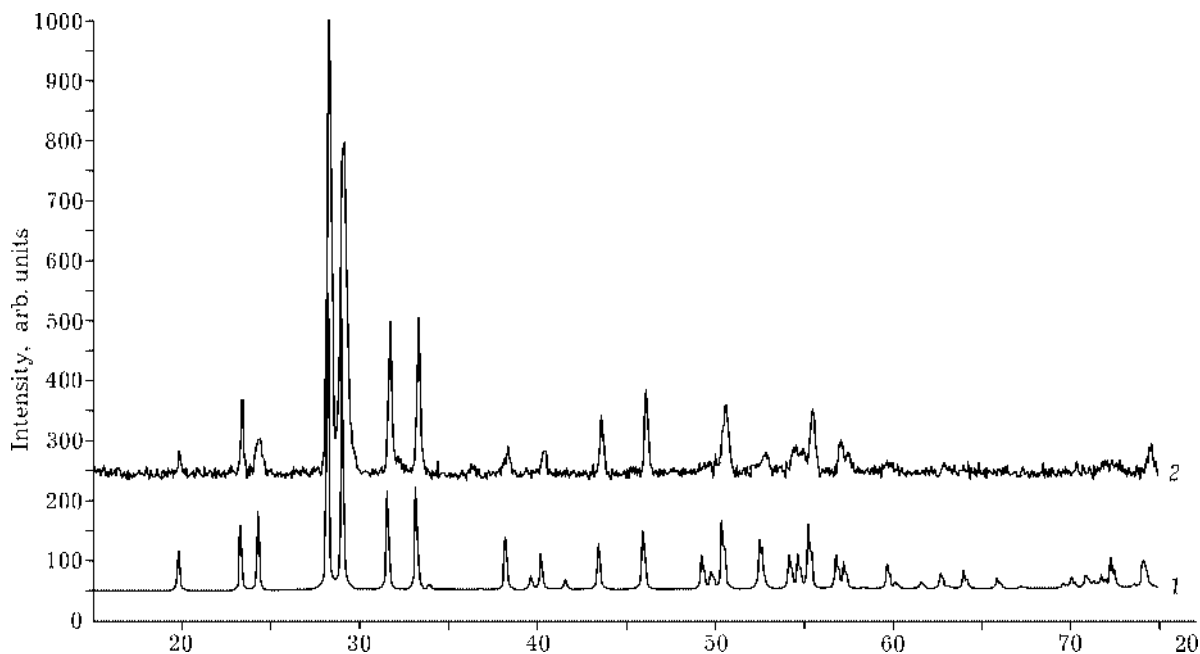


Fig. 4. Diffraction patterns of  $\text{La}_2\text{O}_3 - \text{Ta}_2\text{O}_5$  sample after MCA and subsequent calcination at 1270 K (2) in comparison with theoretical diffraction patterns of  $\text{LaTaO}_4$  (1).

## CONCLUSIONS

Thus, a new convenient method to synthesize tantalates of rare-earth metals is found. The simplicity of the proposed method is shown in a comparative scheme.

Known method:

- $\text{Y}_2\text{O}_3 + \text{Ta}_2\text{O}_5$ , heating up to 1000 °C, homogenization;
- heating up to 1050 °C, 5–10 h, homogenization;
- heating up to 1100 °C, 5–10 h, homogenization;
- heating up to 1150 °C, 5–10 h, homogenization;

– heating up to 1300 °C, 5–10 h;

– classification by the sizes;

– grinding of a large fraction.

New method:

–  $\text{Y}_2\text{O}_3 + \text{Ta}_2\text{O}_5$ , MCA;

– heating up to 1000 °C, 3 h.

Advantages of the new method are:

1. Decrease of temperature of synthesis with 1300 up to 1000 °C.
2. Cutting of time of synthesis from 30–70 h till 3 h.
3. Decrease of the consumption of energy.

Lower energy consumption is confirmed by an approximate calculation. The calculation is made for 1 kg of tantalates with activation in APF planetary mill and furnace capacity of 3 kW h during annealing.

The known method:

annealing – 3 kW  $\cdot$  30–70 h = 90–210 kW h.

New method:

MCA – 11 kW  $\cdot$  0.5 h/0.5 kg = 11 kW h;

annealing – 3 kW  $\cdot$  3 h = 9 kW h;

total – 20 kW h.

This calculation shows that energy consumption in case of the new method is 5–10 times lower. In practice, these values must differ even more because the calculation did not take account of substantial energy consumption for

grinding every 5–10 h according to the above-shown scheme.

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