

Peculiarities of the solid-state synthesis of yttrium and gadolinium orthovanadates raw material

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Present research deals with exploration of the kinetics of chemical interaction between yttrium or gadolinium oxide and vanadium (V) oxide. It was shown that in the temperature range up to 600°C the limiting stage of the orthovanadate synthesis is chemical interaction, and in the temperature range from 600°C to 800°C the limiting stage is diffusion of the starting oxide through the layer of the chemical interaction product. Optimal mode of the solid-state synthesis of the yttrium or gadolinium orthovanadates from the starting oxides was determined.

Keywords: rare earth orthovanadate, solid-state synthesis, transformation degree, Cz-growth.

Представлены результаты исследования кинетики химического взаимодействия между оксидами иттрия или гадолиния и оксидом ванадия (V). Показано, что в температурном интервале до 600°C лимитирующей стадией синтеза ортованадата является химическое взаимодействие, а в температурном интервале от 600°C до 800°C лимитирующая стадия — это диффузия исходных оксидов через слой продукта химической реакции. Определен оптимальный режим твердофазного синтеза ортованадатов иттрия и гадолиния.

Особливості твердофазного синтезу шихти ортованадатів ітрію та гадолінію.
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Наведено результати дослідження кінетики хімічної взаємодії між оксидами ітрію або гадолінію та оксидом ванадію (V). Показано, що у температурному інтервалі до 600°C лімітуючою стадією синтезу ортованадату є хімічна взаємодія, а у температурному інтервалі від 600°C до 800°C лімітуюча стадія — це дифузія вихідних оксидів крізь шар продукту хімічної реакції. Визначено оптимальний режим твердофазного синтезу ортованадатів ітрію та гадолінію.

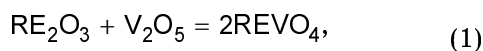
1. Introduction

Yttrium orthovanadate (YVO₄) and gadolinium orthovanadate (GdVO₄) are well-known and widely applied luminescent ma-

terials since 60th of XX century. Doped with different rare earth elements (e.g. Nd³⁺, Tm³⁺, Ho³⁺, Er³⁺ and Yb³⁺) YVO₄ and GdVO₄ are excellent polarizer and laser host materials [1–4]. YVO₄:Eu is the red-emitting

phosphor used in cathode ray tubes and color television [5, 6].

In few recent years the undoped rare earth orthovanadates have been proposed as scintillation materials with slow intrinsic luminescence related to the emission of VO₄-complexes [7, 8]. Bulk single crystals were obtained successfully by the Czochralski technique (Cz), but some difficulties revealed during the crystal growth process. At first, at Cz-growth raw materials with content of the impurity phases and traces of the starting oxides less than 1 wt % in total are desirable. At second, uncontrolled evaporation of vanadium (V) oxide from the melt as well as reduction of vanadium (V) oxide to vanadium (III) oxide is inherent to these compounds [8, 9]. Evaporation of vanadium (V) oxide from the melt associated with the substantial difference of the melting points between vanadium (V) oxide and yttrium or gadolinium orthovanadates: 680°C, 1800°C and 1810°C, respectively, leads to the violation of melt stoichiometry. Reduction of the vanadium (V) oxide causes the appearance of optical imperfections — scattering centers or impurity phases — in the grown crystal due to formation of the metavanadate (REVO₃) phase and the phases depleted with oxygen (4RE₂O₃·V₂O₅ or 5RE₂O₃·V₂O₅) [10]. That is why in the case of Cz-growth the rare earth orthovanadate phase has to be obtained with content of the impurity phases and traces of the starting oxides less than 1 wt.% in total. For this purpose solid-state synthesis with different modifications or sol-gel method has been usually used [11–14]. The present research is focused on the solid-state synthesis of the rare earth orthovanadates from the oxides as starting compounds. The resultant equation of the chemical reaction can be presented as follows:



where RE = rare earth element. In literature we have found different modes of the rare earth orthovanadates solid-state synthesis ranging from calcination at 630°C for 92 h [11] to calcination at 1000–1200°C for 1–2 h [15]. It is worth to note that only one among these works [12] is devoted to exploration of kinetics of the chemical interaction between the rare earth oxide and vanadium (V) oxide.

This research is aimed to explore kinetics of the chemical interaction between the rare

earth oxide, in particular, yttrium or gadolinium oxide, and vanadium (V) oxide to determine optimal mode to run the solid-state synthesis of yttrium and gadolinium orthovanadates from the starting oxides. As a result the sintered raw material for Cz-growth with content of the impurity phases and traces less than 1 wt % in total has to be obtained.

2. Experimental

2.1. Sample preparation

Y₂O₃, Gd₂O₃ (Stanford Materials Co, USA) and V₂O₅ (ReaChim, Russia) with purity not worse than 4N were used as starting materials. The starting oxides were pre-annealed to remove absorbed moisture and CO₂ at 1100°C and 500°C for rare earth oxides and vanadium oxide, respectively, weighted in composition with molar ratio of compounds RE₂O₃:V₂O₅ = 1:1, where RE = Y or Gd, and afterwards mixed in agate mortar with absolute ethanol (C₂H₅OH). Ethanol was added in the value approximately 10 % of the total volume of the mixture. Mixing was kept on until complete evaporation of ethanol from the mixture. The mixtures were pressed into pellets of 10 mm dia., then the pellets were calcined in air at temperatures from 400°C up to 800°C during 8 hours.

2.2. XRD analysis of the samples

XRD studies of yttrium and gadolinium orthovanadate samples were carried out using an automated powder Siemens D 500 diffractometer (the Bragg-Brentano geometry, 2θ range 5° to 125°, step-scanning mode, Δ2θ = 0.02°, counting time of 10 sec). Rietveld analysis [16] of the samples was performed with FullProf&WinPLOTR program package [17] using the crystal structure data given in [18–20].

3. Results and discussion

Content of the orthovanadate phase and starting oxides in the samples, cell parameters and transformation degree of the rare earth oxides in the orthovanadates samples after calcination at different temperatures are presented in Table. The interesting result was observed with the gadolinium orthovanadate samples after solid-state synthesis: slight content of the vanadium oxide in the lower oxidation state (V₃O₇) were detected. Consequently, vanadium was reduced while interaction between gadolinium oxide and vanadium (V) oxide is carried out,

Table. Content of the orthovanadate phase and starting oxides in samples, cell parameters and transformation degree

Sample	Calcination temperature, °C	Phase	Content, mol %	Transformation degree	Cell parameters		
					a , Å	c , Å	V , Å ³
GdVO ₄	400	GdVO ₄	34.73	–	7.2054(8)	6.3485(1)	329.61(8)
		Gd ₂ O ₃	35.79	0.3266			
		V ₂ O ₅	8.39	–			
		V ₂ O ₅	21.09	–			
GdVO ₄	500	GdVO ₄	43.36	–	7.2078(4)	6.3482(4)	329.81(3)
		Gd ₂ O ₃	24.04	0.4742			
		V ₂ O ₅	6.69	–			
		V ₂ O ₅	25.91	–			
GdVO ₄	600	GdVO ₄	86.37	–	7.2098(1)	6.3471(1)	329.935(8)
		Gd ₂ O ₃	4.40	0.9075			
		V ₂ O ₅	9.23	–			
GdVO ₄	700	GdVO ₄	92.06	–	7.2109(1)	6.3468(1)	330.025(7)
		Gd ₂ O ₃	2.43	0.9499			
		V ₂ O ₅	5.53	–			
GdVO ₄	800	GdVO ₄	100	1	7.2110(1)	6.3467(1)	330.025(7)
YVO ₄	400	YVO ₄	3.13	–	7.1116(12)	6.2816(24)	317.27(25)
		Y ₂ O ₃	48.50	0.0313			
		V ₂ O ₅	48.37	–			
YVO ₄	500	YVO ₄	25.68	–	7.1132(2)	6.2902(3)	318.27(25)
		Y ₂ O ₃	39.73	0.2443			
		V ₂ O ₅	34.59	–			
YVO ₄	600	YVO ₄	90.86	–			
		Y ₂ O ₃	4.81	0.9042			
		V ₂ O ₅	4.33	–			
YVO ₄	700	YVO ₄	97.48	–	7.1171(1)	6.2881(1)	318.525(4)
		Y ₂ O ₃	1.03	0.9793			
		V ₂ O ₅	1.49	–			
YVO ₄	800	YVO ₄	99.29	–	7.1174(1)	6.2882(1)	318.553(4)
		Y ₂ O ₃	0.71	0.9858			

and in this red-ox reaction the gadolinium-containing compound is an oxidant. But, according to the values of the standard potential of electrode reaction for gadolinium and yttrium, yttrium with standard potential Y/Y^{3+} equal to -2.372 V possesses higher oxidation ability than gadolinium with standard potential Gd/Gd^{3+} equal to -2.397 V. This contradiction between the experimental results and values of the standard potential of the electrode reaction requires additional analysis and discussion, which is out of scope of the present paper.

The transformation degree was determined for yttrium or gadolinium oxides and was calculated according to formulae (2) due to the chemical stability of these compounds in the temperature range under study:

$$\alpha_i = N_i / N_{i,starting} \quad (2)$$

where α_i is transformation degree, N_i is amount of i -component that reacts and composes the product of the reaction, mol;

$N_{i,starting}$ is starting amount of i -component, mol.

It is worth to note that with increasing of the orthovanadate phase content in the samples the cell parameters tend towards those determined for the orthovanadates previously: $a = 7.123$ Å, $c = 6.29$ Å for YVO₄ and $a = 7.211$ Å, $c = 6.350$ Å for GdVO₄ [20]. As one can see, with increasing of the temperature from 400°C to 600°C content of the orthovanadate phase substantially increases and reaches 90 wt %. Note the steepest increase of the orthovanadate phase content as temperature is raised from 500°C to 600°C. Such behavior can be explained as follows: when the synthesis temperature is approached to the melting temperature of vanadium (V) oxide (680°C), the reaction substantially accelerates. From one hand, it is due to more efficient transfer of the starting components to the surface of the chemical interaction. From the other hand, significant enhancement of the contact surface between the components takes

place. With the following increase of the temperature from 600°C to 800°C content of the orthovanadate phase rises further by about 10 wt % (up to 100 wt %). Also with increasing of the synthesis temperature the transformation degree of the rare earth oxide tends to 1. Dependences of the transformation degree of the rare earth oxides on synthesis temperature are depicted in Fig. 1.

For better understanding of kinetics of the interaction between rare earth oxides and vanadium oxide another parameter — completeness degree of the reaction — was evaluated with the following formulae:

$$\chi = (N_i' - N_{i,starting})/\beta_i, \quad (3)$$

where χ is completeness degree of the reaction; N_i' is amount of i -component in the mixture of starting compound at the time τ , mol; $N_{i,starting}$ is starting amount of i -component, mol; β_i is stoichiometric coefficient for i -component in equation of the chemical reaction. In other words, the difference $N_i' - N_{i,starting}$ in (3) is equal to N_i in (2), and completeness degree of the reaction and transformation degree of the compound are interdependent as the follows:

$$\alpha_i = \beta_i \cdot \chi / N_{i,starting}. \quad (4)$$

For rare earth oxides in the chemical reaction equation (1) it gives:

$$\alpha_i = \chi / N_{i,starting}. \quad (5)$$

Equation for the completeness degree calculation (3) can be written in the next manner:

$$(N_i' - N_{i,starting}) = \chi \cdot \beta_i. \quad (6)$$

Let us designate $N_i' - N_{i,starting}$ as ΔN_i , then

$$\Delta N_i = \chi \cdot \beta_i \quad (7)$$

or

$$dN_i = \beta_i \cdot d\chi. \quad (8)$$

If to divide the both parts of equation (8) by $Vd\tau$:

$$dN_i/Vd\tau = \beta_i \cdot d\chi/Vd\tau, \quad (9)$$

left part defines the expense rate of i -component, R_i , while $d\chi/Vd\tau$ determines the rate of chemical interaction, r_i . We can write down the following equation demonstrating connec-

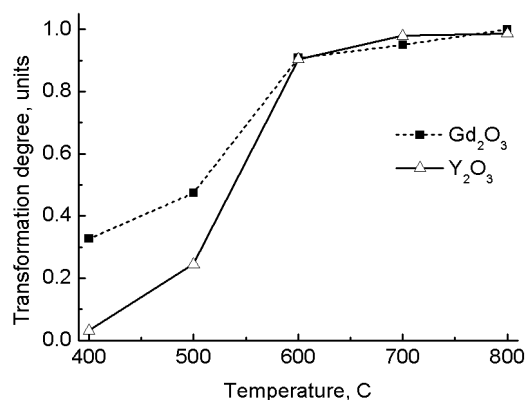


Fig. Dependence of the transformation degree of yttrium and gadolinium oxides on synthesis temperature.

tion between rate of the chemical interaction and expense rate of i -component:

$$R_i = \beta_i \cdot r_i. \quad (10)$$

As was stated above, $r_i \equiv \chi$, hence we can presume that $r_i \equiv \alpha_i$. In other words, substantial rise of the rare earth oxide transformation degree defines an increase of the chemical interaction rate. In Fig. substantial increase of the transformation degree at 400°C – 600°C and weak rise of the transformation degree at 600°C – 800°C is observed. Thus, we can suppose that at 400°C – 600°C the limiting stage of the solid-state synthesis is the chemical interaction between the starting compounds. At 600°C – 800°C the limiting stage of the solid-state synthesis is diffusion of the starting oxide through a layer of the chemical interaction product. This statement can be interpreted as the follows: at temperatures of the solid-state synthesis below 600°C the rate of the chemical reaction is very low and the chemical interaction proceeds very slowly. The higher temperatures are necessary to carry out the solid-state synthesis. Also it is worth to note that our experimental results demonstrate substantial differences with the previously published results: in [12] it was shown that the interaction between yttrium or gadolinium oxide and vanadium (V) oxide is completed (i.e. transformation degree of the yttrium or gadolinium oxide equals 1) after the calcination at 700° – 900°C for 5 min.

According to our experimental results, the calcination at 800°C for 8 h is the optimal mode for the solid-state synthesis of yttrium or gadolinium orthovanadates from the starting oxides.

4. Conclusions

Peculiarities of the solid-state synthesis of yttrium and gadolinium orthovanadates from starting oxides were explored. It was shown that in the temperature range up to 600°C the limiting stage of the orthovanadate synthesis is chemical interaction, and at 600°–800°C the limiting stage is diffusion of the starting oxide through the layer of the chemical interaction product. It was determined that calcination of the starting oxides mixture at 800°C for 8 h is the optimal mode for the solid-state synthesis of yttrium or gadolinium orthovanadates from the starting oxides.

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