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PHASE FORMATION IN NEODYMIUM TANTALATE BASED FLUX SYSTEMS

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The complex systems Nd_2O_3-Ta_2O_5-$Li_2B_4O_7$, Nd_2O_3-Ta_2O_5-$K_2B_4O_7$, Nd_2O_3-Ta_2O_5-KB_5O_8 and Nd_2O_3-Ta_2O_5-$K_2Mo_3O_{10}$-B_2O_3 are considered in light of the possibility of various structure formation in the field of existing melts. Phase formation was estimated through spontaneous nucleation of previously overheated fluxed melts, mostly, near the lines corresponding to the initial molar ratios Nd_2O_3:Ta_2O_5 equal to 1:1, 1:3 and 1:7. As a result, the crystalline $NdTa_7O_{19}$ (NHT), $Nd_{0.33}TaO_3$, $Nd_{1.67}(TaO_3)_5$, $NdTaO_4$, $KTaO_3$ and $LiTaO_3$ phases have been obtained. This study was aimed at gaining an understanding of correlation between the starting composition of the above systems and structures of the phases obtained, taking into account the regularities related to crystal chemistry. Attention was paid to crystallization of NHT in complex systems.

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1. Introduction

Current development in miniature optical components leads to extensive study of bulk crystals with high concentration of active ions as well as single crystal layers which can be used, for example, as active waveguides with different pumping configurations for laser or amplifier applications. In this connection, the complex systems Nd_2O_3-Ta_2O_5-$Li_2B_4O_7$, Nd_2O_3-Ta_2O_5-$K_2B_4O_7$, Nd_2O_3-Ta_2O_5-KB_5O_8 and Nd_2O_3-Ta_2O_5-$K_2Mo_3O_{10}$-B_2O_3 are a base for flux growth of neodymium heptatantalate $NdTa_7O_{19}$ (NHT) crystals as a laser medium having high neodymium concentration and other tantalates with good thermal and chemical stability [1]. These materials can have large device potential, especially, due to the possibility of wide isomorphous substitution in the rare earth positions.

For the first time, NHT was synthesized by solid state reactions [2] and its structure was determined as tetragonal [3]. However, owing to different evaporation rates of neodymium and tantalum oxides, only non-stoichiometric solids could be obtained. Later, the NHT crystals were grown by flux method and their structure was refined in sp.gr. $P6_3/mcm$ with lattice constants: $a=b=6.219(1)$ Å, $c=19.95(2)$ Å [4]. The optical spectra of NHT single crystals have also been measured [5]. These spectra are strongly affected by the presence of optically active ions at different non-equivalent optical centres. The number of components of the low temperature absorption and emission bands often exceeds that expected from the crystal field splitting of the electronic states of a single Nd^{3+} ion. Taking into account the spectroscopic measurements, it can be concluded that the Nd-heptatantalate is a promising material with device potential. On the other hand, it was preliminary estimated that (001) GaN plane is similar to the (001) plane of NHT containing trigonal antiprisms populated with Nd and Ta atoms in the ratio 1:1.

In this paper are presented the recent results on phase formation in complex neodymium-tantalate based systems and the effect of the flux composition on the morphology of NHT crystals is

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considered. This study was undertaken within the scope of a programme to gain an understanding of correlation between the growth conditions, composition, structure, morphology and device potential of tantalate crystals as well as to search and develop alternative substrates for miniature optical components.

2. Experimental procedure

Phase formation in complex systems Nd_2O_3-Ta_2O_5-$Li_2B_4O_7$, Nd_2O_3-Ta_2O_5-$K_2B_4O_7$, Nd_2O_3-Ta_2O_5-KB_5O_8 and Nd_2O_3-Ta_2O_5-$K_2Mo_3O_{10}$-B_2O_3 in the field of existing melts was estimated through spontaneous nucleation of previously overheated fluxed melts, mostly, near the lines corresponding to the initial molar ratios Nd_2O_3:Ta_2O_5 equal to 1:1, 1:3 and 1:7. NHT single crystals were grown from fluxed melts by spontaneous nucleation as well, basing on the complex system $K_2Mo_3O_{10}$-B_2O_3. Starting chemicals were the followings: Nd_2O_3 (3N), Ta_2O_5 (3N), $Li_2B_4O_7$ (2N), $K_2B_4O_7$ (2N), KB_5O_8 (2N) and $K_2Mo_3O_{10}$-B_2O_3. Potassium trimolybdate was previously synthered at 550°C using K_2MoO_4 (2N) and H_2MoO_4 (2N) according to the following reaction:

$$K_2MoO_4+2H_2MoO_3 = K_2Mo_3O_{10}+H_2O\uparrow$$

Crystal growth experiments are divided into two phases. At the first stage, the concentration of NHT in starting fluxed melts varied from 15 to 60 mol% but Nd_2O_3/Ta_2O_5 were within 1:1-1:25 and the certain $K_2Mo_3O_{10}/B_2O_3$ ratio (10:1, in molar fraction) in accordance with previous investigations [6]. In the second cycle, crystallization fields were investigated at constant concentrations of NHT forming components (in the stoichiometric proportion) while $K_2Mo_3O_{10}/B_2O_3$ ratio was varied from 1:1 to 10:1.

Initial mixture was placed into platinum crucibles, and homogenized at 1150°C during 2-24 hours. Then, the temperature was lowered to 900-850°C at a rate of 0.5-5 °C/h. Finally, the charges were cooled down to 400°C at the rate of 10°C/h.

X-ray powder diffraction pattern of solids were obtained in the 2θ range of 14-90° (CoK_α-radiation, $\lambda(K_\alpha)$ = 1.79021Å, Fe filter) using a DRON-UM1 diffractometer. Composition and morphology of grown crystals were studied by analytical scanning electron microscope JSM-5300 with EDS spectrometer Link ISIS.

3. Results and discussion

Nd_2O_3-Ta_2O_5-$Li_2B_4O_7$ system

NHT is the main phase obtained in this system (Fig. 1). These crystals have a plate-like habit and typical size of 2.5 mm. NHT crystals have strongly developed pinacoid {0001}, hexagonal prism $\{10\bar{1}0\}$ and two hexagonal pyramids $\{11\bar{2}1\}$, $\{10\bar{1}2\}$ Morphology of NHT crystals depends on the composition of fluxed melt. The size of pinacoid increases with an increase in $Li_2B_4O_7$ concentration and it is attributed to the increasing of boron-oxygen polymerization, and normal growth rate of the {0001} faces could be suppressed by this process [5].

Nd_2O_3-Ta_2O_5-$K_2B_4O_7$ system

Under the same conditions, replacement of $Li_2B_4O_7$ with $K_2B_4O_7$ leads to simplification of phase formation in the system (Fig. 2). In the vicinity of the $K_2B_4O_7$-Ta_2O_5 line, the charge does not melt at 1150°C if the tetraborate content is less then 60 mol%. When its concentration increases up to 90 mol%, the melt transforms to glass. In all cases, crystallization results in $Nd_{0.33}TaO_3$ and $KTaO_3$ solid phases [6].

Nd_2O_3-Ta_2O_5-KB_5O_8 system

By analogy to the case described above, $Na_{0.33}TaO_3$ and $KTaO_3$ are the main crystalline phases in this system as well (Fig. 3). At the same time, one can determine, besides $Nd_{0.33}TaO_3$, $Nd_{1.67}(TaO_3)_5$ and NHT phases are synthesized, if content of tantalum oxide in the melt is considerable, but decreasing Ta_2O_5 concentration leads to formation $Nd_{0.33}TaO_3$ and $Nd_{1.67}(TaO_3)_5$ solids. In contrast to Li-containing system (field I in Fig. 1) NHT crystals are more isometric. It is not excluded, a difference in morphology of HNT crystals is caused by a lower viscosity of flux melt. Plate-like crystals have been observed only on the «mirror» surface of glass-like melt as a consequence of a higher temperature gradient in the top of cruicible [4].

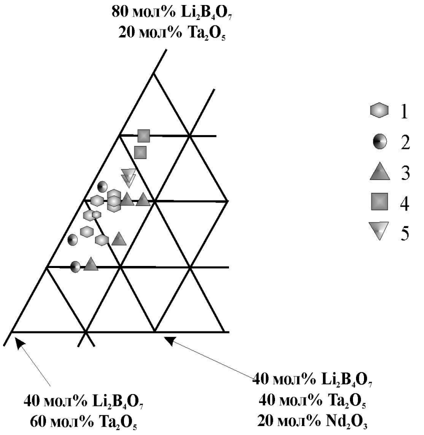

Fig. 1. The field of NHT crystallization in the Nd_2O_3-Ta_2O_5-$Li_2B_4O_7$ system Within the 1140 - 900 °C temperature range: 1 - $NdTa_7O_{19}$ + $LiTaO_3$; 2-$NdTa_7O_{19}$ + $NdTa_5O_{14}$ + $LiTaO_3$; 3 - $NdTa_3O_9$ + $NdTaO_4$; 4-$NdTa_7O_{19}$ + $NdTa_3O_9$+$NdTaO_4$+glass; 5-$NdTa_3O_9$+$NdTaO_4$+glass [5].

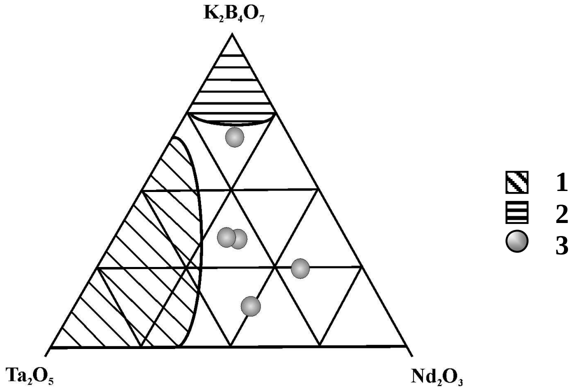

Fig. 2. Phase formation in the Nd_2O_3-Ta_2O_5-$K_2B_4O_7$ system within the 1150-900 °C temperature range: 1-the field of partial melting; 2-glass formation; 3- $Nd_{0.33}TaO_3$ + $KTaO_3$ solid phases.

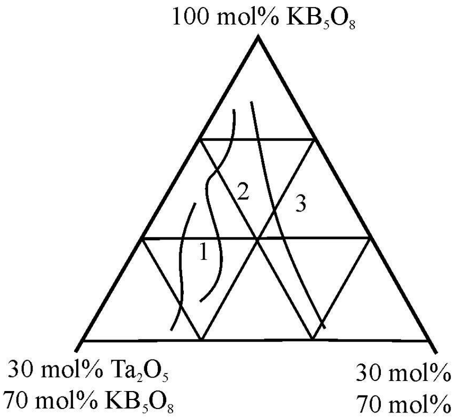

Fig. 3. Phase formation in the Nd_2O_3-Ta_2O_5-KB_5O_8 system within the 1140-850°C temperature range: 1- $Nd_{0.33}TaO_3$+$Nd_{1.67}(TaO_3)_5$+$NdTa_7O_{19}$; 2-$Nd_{0.33}TaO$+$Nd_{0.33}(TaO_3)_5$; 3- $Nd_{0.33}TaO_3$.

Nd_2O_3-Ta_2O_5-$K_2Mo_3O_{10}$-B_2O_3 system

Pseudoternary system based on the $K_2Mo_3O_{10}$-B_2O_3 complex solvent seems to be the most significant to synthesize various crystalline phases (Fig. 4). Neodymium heptatantalate crystallizes mainly in the limits of regions 1, 2 and 3. In contrast to the above systems, there is the monophase region of NHT crystallization (field 1 in Fig. 4). Other two regions are characterized by the presence of subsidiary phases: NHT crystallizes together with $Nd_{0.33}TaO_3$ (field 2), or $Nd_{0.33}TaO_3$ and $NdTaO_4$ with β-fergusonite structure (field 3).

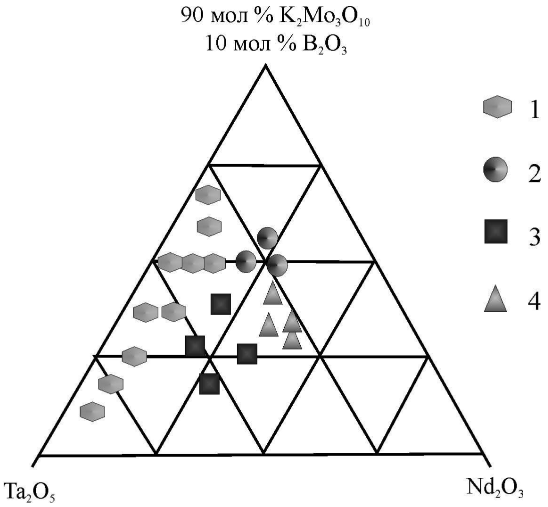

Fig. 4. The field of NHT crystallization in the Nd_2O_3-Ta_2O_5-$K_2Mo_3O_{10}$-B_2O_3 system within the 1150 – 900 °C temperature range: 1-$NdTa_7O_{19}$+Ta_2O_5; 2-$NdTa_7O_{19}$+$Nd_{0.33}TaO_3$+$NdTaO_4$ (β-fergusonite); 3- $NdTa_7O_{19}$+$Nd_{0.33}TaO_3$; 4- $Nd_{0.33}TaO_3$+$Nd_{1.67}(TaO_3)_5$.

However, $Nd_{0.33}TaO_{33}$ crystals grown within the region 2 have characteristic «neodymium» light-lilac colour, but they are light-brown in the field 3. In the first case, NHT crystals are prismatic, but they have plate-like habit in the fields 2 and 3. Lilac needle-like $Nd_{1.67}(TaO_3)_3$ crystals are obtained in the 4 region. An excess of potassium trimolybdate and Ta_2O_5, leads to formation of the multinary oxide $MoTa_{12}O_{33}$. Green transparent Ta_2O_5 crystals with strongly developed growth striations are synthesized in the monophase region of NHT crystallization.

An increase in concentration of Nd_2O_3 in the complex melt promotes to the transformation in the coordinating number of Ta-polyhedrons as well as their polymerization. Step by step, isolated Ta tetrahedra in $NdTaO_4$ with β-fergusonite type of structure are replaced by three-dimensional perovskite–like $Nd_{0,33}TaO_3$ containing tantalum-oxygen octahedra, and then by the framework with 3-, 4- and 5-fold rings in $Nd_{1,67}(TaO_3)_5$. Finally, in crystallization process of $NdTa_7O_{19}$, there is substantial compaction of tantalum-oxygen polyanions in solid phases. On the whole, decreasing Nd_2O_3/Ta_2O_5 ratio is accompanied by the increase in tantalum coordination numbers from 4 up to 6 and 7.

The facetting of NHT crystals is characterized by a small number of simple forms: pinacoid {0001}, hexagonal prism $\{10\bar{1}0\}$ and two hexagonal pyramids $\{11\bar{2}0\}$ and $\{11\bar{2}1\}$. A difference in the morphology of NHT crystals depends on the chemical composition of fluxed melt. Increase in the concentration of $K_2Mo_3O_{10}$ in the $K_2Mo_3O_{10}$-B_2O_3 solvent promotes the development of {0001} faces in NHT crystals (Fig. 4). Apparently, the habit elongated is connected with the entry of Mo ions into the crystals.

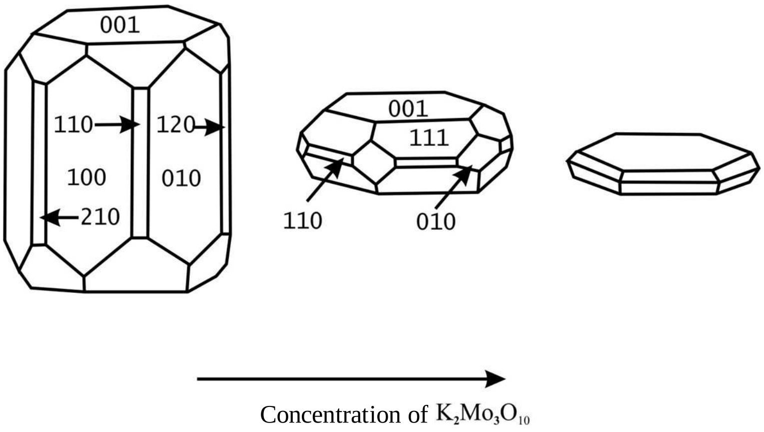

Fig. 5. The influence of concentration of $K_2Mo_3O_{10}$ on the habitus of NHT crystals.

4. Conclusions

The complex systems Nd_2O_3-Ta_2O_5-$Li_2B_4O_7$, Nd_2O_3-Ta_2O_5-$K_2B_4O_7$, Nd_2O_3-Ta_2O_5-KB_5O_8 and Nd_2O_3-Ta_2O_5-$K_2Mo_3O_{10}$-B_2O_3 are considered in light of the possibility for gettimg various structural forms in the field of existing melts. Near the lines corresponding to the initial molar ratios Nd_2O_3:Ta_2O_5 equal to 1:1, 1:3 and 1:7, the crystalline $NdTa_7O_{19}$, $Nd_{0.33}TaO_3$, $Nd_{1.67}(TaO_3)_5$, $NdTaO_4$, $KTaO_3$ and $LiTaO_3$ phases have been obtained. An increase in concentration of Nd_2O_3 in the complex melt leads to transformation in the coordinating number of Ta-polyhedrons as well as their polymerization. On the whole, the decrease of the Nd_2O_3/Ta_2O_5 ratio is accompanied by the increase in tantalum coordination numbers from 4 up to 6 and 7. The phase formation data in the complex pseudoternary system based on potassium trimolybdate and boron anhydrite are updated. Preliminary investigations related to the dependence of NHT morphology on growth conditions are carried out. Increase in the concentration of $K_2Mo_3O_{10}$ in the $K_2Mo_3O_{10}$-B_2O_3 solvent promotes the development of {0001} faces on NHT crystals. For this reason, the study of NHT crystal growth conditions must be continued, in order to obtain this material with a sufficient large size for laser experiments.

Additionally, further efforts will be focused on the neodymium heptatantalate to use it as alternative substrate for epitaxial growth of GaN thin films.

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