High–temperature crystallization of novel rare–earth borate materials: single crystals and thin films

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Abstract. Phase formation has been studied in the complex system YbAl3(BO3)4 - K2Mo3O10 - B2O3 - Yb2O3 within the stability region of YbAl3(BO3)4 (YbAB). The obtained data were compared with those for YAl3(BO3)4 as another end member of the YbAB-YAB solid solutions. Visually transparent (Er,Yb):YAl3(BO3)4 single crystals with a typical size up to 10×10×15 mm3 and crystalline layers were obtained from K2Mo3O10 based fluxed melts. The 1.5 µm emission spectra of (Er,Yb):YAl3(BO3)4 thin films as well as bulk crystals were measured using CW Ti:sapphire laser tuned to 976 nm as a pump source.

1. Introduction
Development of small optical components requires highly efficient single crystals and crystalline layers. They can be used, for example, as compact disk lasers or as active waveguides with different pumping configurations in laser and amplifier applications. In this regard, borate crystals with a general formula RA13(BO3)4 (R = Y; Pr–Lu) are potentially interesting because of their wide isomorphous substitutions [1]. In this family, YAl3(BO3)4 (YAB) crystal is a well-known laser host for Yb and Nd ions [2-3]. YAB bulk crystals and thin layers, co-doped with Yb and Er, also demonstrate promising properties for telecommunications, medical and range-finding applications [4-6]. Recently, (Er,Yb):YAB was proposed as a laser material, which can potentially generate multi-watt powers under diode-laser pumping at ~980 nm. CW output power of 1 W with a slope efficiency of 35% was obtained, but the output power was limited by the available pump source [4,5]. Mode-locked regime has been realized with pulse duration of about 4 ps and average output power of 270 mW [6].

Flux growth technology of YAB crystals is well known and is based on the pseudo-quaternary YAB - K2Mo3O10 - B2O3 - Y2O3 system [7]. As for other end member of (Yb,Y)Al3(BO3)4 solid solutions, i.e., YbAl3(BO3)4 (YbAB), its crystallization conditions from similar complex high-temperature solutions needs to be studied.

Here, we discuss recent results on phase formations in the complex system YbAl3(BO3)4 - K2Mo3O10 - B2O3 - Yb2O3, as well as on the growth of (Er,Yb)–codoped YAB bulk crystals and (Er,Yb):YAB crystalline layers. We also present the 1.5 µm emission spectra of thin films and bulk crystals.
2. Experimental details

Phase relationships in the pseudo-quaternary YbAB - K₂Mo₃O₁₀ - B₂O₃ - Yb₂O₃ system were studied in the temperature range 1000-1150 °C by a spontaneous nucleation approach for two cross sections corresponding to 15 and 20 wt% of YbAB. Formation of solid phases was revealed for regions of YbAB stability and existence of the melt in the studied system. The data are presented as projections on the temperature level at 1000 °C.

The complex solvent, containing potassium trimolybdate K₂Mo₃O₁₀ with an excess of boron and rare earth oxides, was used in all runs. Starting chemicals (at least 99.99% and 99.999% purity for rare earths and other materials, respectively) were Y₂O₃, Yb₂O₃, Er₂O₃, Yb₂O₃, Al₂O₃ and B₂O₃, but K₂Mo₃O₁₀ was previously sintered from K₂MoO₄ and H₂MoO₄ at 650 °C according to the reaction:

\[
K₂MoO₄ + 2H₂MoO₃ \rightarrow K₂Mo₃O₁₀ + 2H₂O
\]

The starting charge was mixed and placed into a platinum crucible and homogenized at 1150 °C in a high-temperature furnace for 24 – 48 h. The temperature at the bottom of the crucible was kept 2–3 °C higher than at the melt surface. The flux components were varied from 30 to 85 mol% (K₂Mo₃O₁₀), 10 to 70 mol% (B₂O₃) and 0 to 20 mol% (Yb₂O₃). Then, the temperature was lowered at a rate of 0.5–1 °C/h to 1000 °C (15 wt% YbAB) or to 1050 °C (20 wt% YbAB). After this procedure, the crucibles were quickly cooled down to 300 °C and removed from the furnace. The solid phases were released from the solidified melt by dissolution in hot diluted hydrochloric acid, in order to identify them by X-ray powder diffraction.

Temperature dependence of YbAB solubility was studied in the range of 8 - 14 mol% for the fluxes (I) 55 mol% K₂Mo₃O₁₀, 45 mol% B₂O₃ and (II) 55 mol% K₂Mo₃O₁₀, 40 mol% B₂O₃, 5 mol% Yb₂O₃ by a probe technique. The saturation temperatures were found from the experimental data on changes in weight and micro-relief of the probe seeds after soaking for a period from 10 min to several hours in fluxed melts, depending on the deviation from their equilibrium points.

Single crystals of ErₓYbᵧY₁₋ₓ₋ᵧAl₃(BO₃)₄ with x = 0.005 to 0.015 and y = 0.07 to 0.15 in the starting crystalline substances, as well as pure YAl₃(BO₃)₄ single crystals, were obtained by dipping seeded solution growth (DSSG). The fraction of YAB and (Er,Yb):YAB crystalline substances in the starting solutions was 17 wt%. Before DSSG, the saturation temperatures of fluxed melts were determined by a probe technique as 1060–1080 °C depending on the dopant concentration. A “point” YAB seed of 0.3×0.3×1.0 mm³ size was dipped into fluxed melt. During the crystal growth, supersaturation was kept within the temperature range 1080–1000 °C by the cooling of fluxed melts at a rate 0.2–5 °C/day following the experiments on the solubility and crystallization kinetics. At the end of the growth process, the crystal was pulled out and cooled to the room temperature within several days.

Thin films were grown under similar conditions, using liquid phase epitaxy (LPE). At the beginning of epitaxial growth, the YAB substrate was slowly dipped into the solution at the temperature 1 °C higher than saturation point, T_sat. After 10–20 min, the temperature was decreased to 3–12 °C below T_sat and kept at this level for 9–36 h in order to grow the (Er,Yb):YAB layers depending on supercooling of the fluxed melt and on expected thickness of the layer, as it follows from their growth kinetics. Then, the substrate with deposited film were slowly pulled out, cooled to the room temperature and released from the crystallized melt by dissolution in hydrochloric acid, distilled water and ethanol.

Substrate choice is crucial for LPE growth. It should match the material to be deposited both in the lattice parameters and in the thermal expansion coefficient. Otherwise strains are introduced into the film and cracks occur if the mismatch is large. Furthermore, differences in refractive indices between the substrate and the active layer are important because YAB crystalline thin layers doped with Er³⁺ and Yb³⁺ can be applied in active waveguide devices, such as planar and channel waveguide lasers. In homoepitaxy, the lattice parameters, melting temperatures, and thermal expansion coefficients are
matched between the substrate and film. However, it is not suitable for making waveguides as the film should have higher refractive index than the substrate. According to ref. [8], substitution of Y³⁺ by Yb³⁺ up to 7 at% increases the ordinary and extraordinary refractive indices by ~0.002 and 0.001, respectively. In this respect, single crystals of YAB are an optimal substrate for the LPE of (Er, Yb):YAB layers.

The substrate wafers with sizes up to 0.7–10 mm² and thickness of 0.5–1.5 mm were cut from undoped DSSG–grown YAB single crystals parallel to rhombohedron face and mechanically polished. The X-ray powder diffraction patterns were obtained using DRON-1UM and STOE STADIMP diffractometers. The composition, homogeneity and external morphology of single-crystal layers were studied with an analytical scanning electron microscope (ASEM) JSM-5300 + Link ISIS. Microprobe analysis of unpolished samples was performed with an accuracy of 0.2-0.3 wt%. A Cameca analyzer was used for study layers with a minor dopant concentration. The distribution coefficient was calculated as

\[ K_d = \frac{C_{\text{cryst}}}{C_{\text{dissRAYB}}} \]

where \( C_{\text{cryst}} \) is the content of element \( R \) (\( R = \text{Y; Pr–Lu} \)) in RYAB grown epilayers and \( C_{\text{dissRAYB}} \) is the \( R \) concentration in the borate crystalline of the fluxed melt.

Room-temperature polarized absorption spectra of LPE-grown (Er,Yb):YAB thin films in the 1 µm spectral region were measured using a Cary-5000 spectrophotometer. The 1.5 µm emission spectra of Er,Yb:YAB thin film as well as of bulk crystal were obtained using CW Ti:sapphire laser tuned to 976 nm as a pump source. The laser beam was focused using wide-aperture 10× microscope objective. The fluorescence was collected by the same objective, reflected by the selective mirror and focused on the slits of a 1-m monochromator. It was detected by a Si photodiode and processed by a lock-in amplifier. The spectral response of the system was calibrated using a stabilized tungsten lamp. The surface and morphology of the films were examined with Leica DM 4000 M optical microscope equipped with a Leica DFC-290 camera. The optical magnification was varied from 40× to 500×. Digital interference contrast (DIC) technique was used to improve the contrast of the small surface irregularities.

3. Results and discussion

No YbAB single-phase crystallization was found in the pseudo-quaternary 20 wt% YbAl₃(BO₃)₄ - 80 wt% (K₂Mo₃O₁₀·B₂O₃·Yb₂O₃) system in the temperature range 1150-1050 °C. YbAB and YbBO₃ orthoborates co-crystallize in region II (figure 1a). Only small hexagonal YbBO₃ plates and needle-shaped Al₅(BO₃)O₆ orthotrichorate crystals were observed in the regions III and IV, respectively.

As for the 15 wt% YbAB cross-section of the above complex system, single-phase YbAB crystallization was revealed upon lowering the temperature from 1100 to 1000 °C (figure 1b). Its field is limited by variations of the Yb₂O₃ and B₂O₃ contents in the flux from 5 to 10 mol% and 20 to 40 mol%, respectively. In the region I, isometric YbAB crystals exhibit well-developed \{10\overline{1}1\}, \{1\overline{1}2\overline{0}\} and \{2\overline{1}\overline{1}0\} faces. In this case, the saturation points of YbAB insignificantly increase with an excess of ytterbium oxide in the complex K₂Mo₃O₁₀·B₂O₃·Yb₂O₃ solvent (figure 2a). On the other hand, these temperatures decrease substantially with increasing B₂O₃ concentration in the K₂Mo₃O₁₀·B₂O₃ solvent (figure 2b). Only YbBO₃ orthoborate crystallizes in the regions III (figure 1b), but increasing Yb₂O₃ content up to 20 mol% in the solvent leads to a considerable increase in the melting temperature of starting load (figure 2b, region V).

Comparative analysis of phase relationships in the YbAB (15 wt%) and YAB (17 wt%) based systems indicates that R₂O₃ concentration in the K₂Mo₃O₁₀·B₂O₃·R₂O₃ solvent seems to be not higher than 10 mol%. The regions of single phase YbAB and YAB crystallization coincide in a narrow range (overlapping field in figure 3).

The visually transparent YAB and (Er,Yb):YAB crystals were obtained with a typical size up to 10×10×15 mm³ and 8×8×12 mm³, respectively. YAB crystals are colorless, but the (Er, Yb):YAB samples have the characteristic for erbium light pink color. The average Er and Yb effective distribution coefficient is 0.84 as a consequence of minor differences in the sizes of Y³⁺, Er³⁺ and Yb³⁺ cations.
Figure 1. Phase relationships in the systems 20 wt% YbAB–80 wt% (K₂Mo₃O₁₀-B₂O₃-Yb₂O₃) (a) and 15 wt% YbAB–85 wt% (K₂Mo₃O₁₀-B₂O₃-Yb₂O₃) (b) in the temperature range 1000-1150 °C: (I) ● - YbAB; (II) ▼ - YbAB+YbBO₃; (III) ▼ - YbBO₃; (IV) ● - Al₅(BO₃)O₆; (V) ■ - YbAB, as a result of solid state reactions (■ and x loads do not melt at 1150 °C); (VI) ○ - glass forming melt; (VII) ■ - separating melt.

Figure 2. YbAB saturation points in 15 wt% fluxed melt depending on the Yb₂O₃ (a) and B₂O₃ (b) concentrations in the complex solvents.
The observed growth rates were similar for all the studied Er\(_{0.015}\)Yb\(_{0.11}\)Y\(_{0.875}\)Al\(_3\)(BO\(_3\))\(_4\) and Yb\(_{0.1}\)Y\(_{0.9}\)Al\(_3\)(BO\(_3\))\(_4\) single-crystal layers, because the presence of a small amount of dopant does not change the development of the layers. Thus the LPE growth can be considered as almost homoepitaxial. The surface morphology was quite good and flat over large areas. There were no visible inclusions in the layers. Though the polished edge looks optically good, the as-grown surface has some imperfections and cracks. All the surface irregularities are smaller than 50 \(\mu\)m (figure 4). The border between the doped film and the undoped substrate is clearly visible in polarized light (figure 5).

Room-temperature polarized absorption and emission spectra of (Er,Yb):YAB bulk crystal and thin film are shown in figures 6 and 7, respectively. The spectra look very similar; neither absorption nor emission peaks of the LPE-grown layers are broadened in comparison with the bulk crystal. The similarity of the absorption and fluorescence spectra of (Er,Yb):YAB bulk crystals and LPE-grown thin films indicates good crystallinity of the latter.
5. Conclusions
The region of primary YbAB crystallization was revealed for 15 wt% of YbAB cross section in YbAB-K_2Mo_3O_10-B_2O_3-Yb_2O_3 pseudo-quaternary system. The saturation points of YbAB containing fluxed insignificantly increase with increasing ytterbium oxide and decreasing B_2O_3 concentration in the flux. Phase relationships are similar in both ytterbium and yttrium systems. The regions of single-phase YbAB and YAB crystallization somewhat overlap each other in the temperature range 1000 – 1150 °C. Most preferable fluxes for crystal growth of YbAB - YAB solid solutions appear as: (I) 55 mol% K_2Mo_3O_10, 45 mol% B_2O_3 and (II) 55 mol% K_2Mo_3O_10, 40 mol% B_2O_3, 5 mol% R_2O_3. Optically transparent YAB and (Er,Yb):YAB crystals with sizes up to 10×10×15 mm³ were obtained by the DSSG technique. (Er,Yb):YAB thin film growth was performed under similar conditions, using liquid
phase epitaxy. The 1.5 µm emission spectra of thin films and bulk crystals were measured using CW Ti:sapphire laser tuned to 976 nm.

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