

# Ytterbium and Erbium Co-doped Rare-Earth Aluminum Borate Crystals as New Materials for Eye-Safe Lasers: Flux Growth and Characterization

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# Contents

Introduction	2
Crystal Growth and Basic Properties	3
Experimental	3
YAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	5
GdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	8
ErAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	8
YbAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	10
$\operatorname{Er:Yb_xGd_{1-x}Al_3(BO_3)_4}$	12
LuAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	17
(Er,Yb):YAB Crystalline Thin Layers	26
RAB Glass-Ceramic Composites	30
Laser-Related Spectroscopy	33
Experimental	33
(Er,Yb):YAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	35
(Er,Yb):GdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	37
(Er,Yb):LuAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	38
(Er,Yb):YAB Crystalline Thin Layers	39
(Er,Yb):RAB Glass-Ceramic Composites	42
Concluding Remarks and Outlook	44
References	44

#### Abstract

Phase relationships in  $RAl_3(BO_3)_4$ -(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>- $R_2O_3$ -B<sub>2</sub>O<sub>3</sub>) pseudo-quaternary systems (R = Y, Gd, Er, Yb, Lu) have been studied in the temperature range

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from 1150 °C to 900 °C, and the results obtained for 25–17 wt.%  $RAl_3(BO_3)_4$  (*RAB*) concentrations were presented graphically as their projections onto the cross section at 900 °C of temperature-composition diagram. Er,Yb co-doped single crystals were grown on dipped "point" seeds. The absorption spectra of (Er,Yb):*RAB* crystals were measured at room temperature. The optical and emission spectrum and lifetime of the  ${}^{4}I_{13/2}$  energy level were determined. From the spectroscopic point of view, Er-Yb co-doped *RAB* material looks promising as a gain medium for compact diode-pumped lasers operating in the 1500–1600 nm eye-safe spectral range.

#### Introduction

More than five decades ago in 1962, Ballman obtained 12 new rare-earth borate crystals:  $RAl_3(BO_3)_4$  (RAB) with R = Y, Nd, Eu, Gd-Er, Yb and  $RCr_3(BO_3)_4$  (R = Sm or Gd), using K<sub>2</sub>SO<sub>4</sub>-3MoO<sub>3</sub> and PbF<sub>2</sub>-3B<sub>2</sub>O<sub>3</sub> fluxes [1]. Based on X-ray powder diffraction studies, these compounds were assigned to the structural type of carbonate mineral huntite, CaMg<sub>3</sub>(CO<sub>3</sub>)<sub>4</sub> (R32 sp.gr.) [2]. In the 1970s and 1980s, NdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (NAB) [3, 4], YAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (YAB) [5], and GdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (GdAB) [6] crystal structures were refined. Unlike huntite structure, which has only trigonal modification, *R*Al-borates exhibit three polytypic forms with space groups *R32*, C2/c, and *C2* [7]. Polytypes demonstrate very similar structures, and it is difficult to identify them using traditional X-ray powder diffraction (XRD) analysis. Hence, these irreversible second-order phase transitions (PTs) were described within the scope of the order-disorder (OD) theory [8].

At the end of the 1980s, it was shown that PrAl-, NdAl-, SmAl-, EuAl-, and GdAl-borate crystals tend to phase transitions from low-temperature rhombohedral acentric modification (low-RAB) into high-temperature monoclinic centrosymmetric phase (high-RAB) at 880-900 °C, 880-900 °C, 1130-1150 °C, 1130-1150 °C, and 1040–1050 °C, respectively, depending on crystal growth conditions [9] (Table 1). These PTs are not sensitive for measurements by differential thermal analysis (DTA). For this reason, taking into account differences in the micromorphology of rhombohedral and monoclinic single crystals [10], a small RAB crystal of nominal composition was dipped into supersaturated fluxed melt at a temperature expected for the phase transition. As a result, the PT temperatures with an accuracy of  $\pm 2-5$  °C were found from the experimental data on changes in microrelief of the probe crystals after their holding in fluxed melts from 10 min to several hours, depending on the fluxed melt deviation from its saturation point. It was also found that RAB crystals melt incongruently in the temperature range of 1170-1290 °C, and they decompose into AlBO<sub>3</sub> and RBO<sub>3</sub> [11] (Table 2), although according to the [12], the NAB melting point measured by the DTA method is  $1150 \pm 5$  °C.

Nowadays, there are a number of borates and their solid solutions with a general formula  $RAl_3(BO_3)_4$  where R = Y, Pr, Nd, Sm-Lu. Since the early 1960s of the last century, they were intensively characterized and attracted much attention as new multifunctional optical materials due to their good chemical, mechanical, and

Borate	Sp.gr.	T <sub>ph.tr.</sub> , °C	Refs.
PrAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	$R32 \rightarrow C2/c$	880–900	[ <b>9</b> ]
	$C2/c \rightarrow C2$	1080	
NdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	$R32 \rightarrow C2/c$	880–900	[ <mark>9</mark> ]
	P6/mmm (P6/m) $\rightarrow$ C2	950 ± 15	[12]
SmAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	$R32 \rightarrow C2/c$	1130–1150	[ <mark>9</mark> ]
EuAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	$R32 \rightarrow C2/c$	1130–1150	[ <mark>9</mark> ]
GdAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	$R32 \rightarrow C2$	1040-1050	[6]

Table 1 Phase transitions (T<sub>ph.tr.</sub>) of *RAB* crystals

	-		(	-	-		
Borate	T <sub>dec</sub> , °C						
YAl	1280	SmAl	1230	TbAl	1265	ErAl	1280
PrAl	1170	EuAl	1235	DyAl	1270	TmAl	1290
NdAl	1190	GdAl	1255	HoAl	1280	YbAl	1290

**Table 2** Decomposition temperatures  $(T_{dec})$  of *RAB* in air [11]

thermal properties and possibilities of wide isomorphic substitutions in *R*-positions of their crystal structure. Also, the non-centrosymmetric low-temperature *R*AB crystals are of most interest as promising solids for both lasing and nonlinear optical applications [13-15].

Among them, YAB [16–19], GdAB [20], and LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (LuAB) [21] crystals were also mainly considered as a host material for laser applications with Yb<sup>3+</sup> and  $Er^{3+}$  dopants which can be used as a novel solid-state matrix for lasing in the eyesafe 1500 nm spectral range.

This chapter summarizes selected results on high-temperature solution growth on dipped seeds (SGDS) and basic structural, compositional, and morphological characterization of *R*AB (R = Y, Gd, Lu) single crystals, including their solid solutions, thin films, and glass-ceramic composites obtained in Moscow State University during the last two decades. Key laser experiments and laser-related spectroscopic investigations of these materials were recently performed in the Center for Optical Materials and Technologies, Belarusian National Technical University.

#### **Crystal Growth and Basic Properties**

#### Experimental

As it was discussed earlier [22], flux systems based on potassium trimolybdate are most acceptable solvents for *R*AB crystal growth by the SGDS method, but it was found that *R*Al-borates dissolve incongruently in the  $K_2Mo_3O_{10}$  melt of nominal composition due to formation of new solid phases, as a result of the interaction between the  $K_2Mo_3O_{10}$  flux and *R*AB compounds. The temperature level for precipitation of different "co-crystallizing" solid phases (Al<sub>5</sub>BO<sub>9</sub>, *R*BO<sub>3</sub>,

 $RAl_2(B_4O_{10})O_{0.5}$ ,  $RK(MoO_4)_2$ ) depends upon the type of borate and its concentration in the fluxed melt.  $Al_5BO_9$  normally appears at 1160–1100 °C,  $RBO_3$  precipitates within 1100–1050 °C, and  $RK(MoO_4)_2$  co-crystallizes below 900 °C. For example, primary crystallization fields of  $RAl_2[B_4O_{10}]O_{0.5}$  (R=Pr, Nd) metaborates are always timed to  $B_2O_3$ -enriched fluxed melts, small needlelike alumino-alumoborate  $Al_5BO_9$  ( $Al_2[Al_3O_6BO_3]$ ) [23] crystals are formed at elevated temperatures, and they act, therefore, as additional centers for RAB nucleation during further cooling process. Also, RAl-borate small crystals can preserve inside these "seeds" in the form of inclusions, strongly deteriorating homogeneity of the crystal grown.

As a result of incongruent *RAB* dissolution, the fluxed melt is enriched both by boron and rare-earth metal oxides, and rare earth oxide components partially go into *RBO*<sub>3</sub> and *RK*(MoO<sub>4</sub>)<sub>2</sub> compounds only below 1100 °C and 900 °C, respectively. For this reason, it is worthwhile to use the Le Chatelier's rule. Following this concept, the below reactions can be shifted to the left by making an excess of  $R_2O_3$  and  $B_2O_3$  components to the initial melt composition, in order to suppress incongruent dissolution of the *RAB* compounds:

(a)  $RAl_3(BO_3)_4 + K_2Mo_3O_{10}$  (melt I)  $\rightarrow Al_5BO_9 + melt II (\sim 1160 ^{\circ}C \rightarrow 1100 ^{\circ}C)$ (b) melt II  $\rightarrow RAl_2(B_4O_{10})O_{0.5} + melt III (\sim 1050 ^{\circ}C \rightarrow 900 ^{\circ}C)$  for R=Pr, Nd (b') melt II  $\rightarrow RBO_3 + melt III (\sim 1100 ^{\circ}C \rightarrow 1050 ^{\circ}C)$  in the case of R= Sm-Lu, Y (c) melt III  $\rightarrow RK(MoO_4)_2 + melt IV (\sim 900 ^{\circ}C \rightarrow 800 ^{\circ}C)$ 

As a further step, therefore, for *R*AB crystal growth from these complicated flux systems, a detailed analysis has been done only for the phases existing in the equilibrium with the complex flux. Together with some simple oxides, more complex compounds were also chosen as components, and pseudo-quaternary *R*AB- $K_2Mo_3O_{10}$ - $B_2O_3$ - $R_2O_3$  (*R*=Y, Gd) systems have been studied [24, 25]. This approach, being methodically rigorous, makes the *R*AB crystal growth technology more lucid and understandable.

The properties of  $K_2Mo_3O_{10}$ -based multicomponent phase diagrams limit the range of studied *RAB* crystallization fields. Most acceptable systems have melting temperatures typically no higher than 1150 °C because of considerable increase in flux evaporation and/or the borate decomposition. The lowest temperature limit (as a rule, about 900 °C) was detained by a substantial decrease in the growth rate of crystals and by the beginning of crystallization of incidental phases.

In crystal growth experiments, the starting chemicals were  $R_2O_3$ ,  $Al_2O_3$ , and  $B_2O_3$ .  $K_2Mo_3O_{10}$  was previously sintered using  $K_2MoO_4$  and  $MoO_3$  at ~650 °C for 24 h according to the scheme:

$$K_2MoO_4 + 2MoO_3 \rightarrow K_2Mo_3O_{10}$$
.

Initially, investigations of these borate phase diagrams were performed through spontaneous nucleation in 10–15 ml Pt crucibles with a slow cooling rate (0.5–1 °C/h) within a given temperature range (usually 1150–900 °C), varying flux compositions from 5 to 10 mol.% for each *RAB* concentration.

The identification of the phases obtained was carried out by means of X-ray diffraction technique (both powder and single crystal methods), using DRON-1UM and STOE STADI MP diffractometers. External morphology and homogeneity of grown single crystals were studied under regular optical microscope as well as by analytical scanning electron microscope (ASEM) JSM-5300 + Link ISIS. Microprobe analysis of unpolished samples was performed within the accuracy of 0.2–0.3 wt.%. A Cameca analyzer was used for study of crystals with a minor dopant concentration. The segregation coefficients ( $K_s$ ) were calculated according to the equation:

$$K_s = C_{\text{cryst}}/C_{\text{dissRAYB}},$$

where  $C_{\text{cryst}}$  is *R* content in as-grown *RAB* crystals and  $C_{\text{dissRAB}}$  is *R* concentrations in the nutrient borate of the fluxed melt.

The data obtained for the regions of *R*AB stability and melt existence in the system studied were represented graphically as projections of all solid phases (including *R*AB and co-crystallizing phases) forming within the temperature interval from 1150 to 900 °C onto the triangle of flux compositions corresponding to the tetrahedron cross section, i.e., to the given *R*AB concentration in each *R*AB- $K_2Mo_3O_{10}$ - $B_2O_3$ - $R_2O_3$  complex fluxed melt. Flux compositions were also plotted on the triangles of *R*AB single-phase crystallization in all pseudo-quaternary systems. As an example, YAB field of primary crystallization from  $K_2Mo_3O_{10}$ -based fluxed melt is shown on Fig. 1. On this way, therefore, flux compositions were identified for single-phase crystallization of all *R*AB studied.

Since no accidental co-crystallizing phases are stable in the *R*AB single-phase regions, the *R*AB solubility curves can be considered as fragments of a pseudobinary system, in which the material to be crystallized and a complex flux are considered to be a repeated fragment of a binary solubility diagram. The dependence of *R*AB solubility on the temperature was studied by a probe method using 130–150 ml Pt crucibles (Fig. 2). The saturation temperatures were found from the experimental data on changes both in weight and microrelief of the probe seeds after keeping in fluxed melts from 10 min to several hours, depending on an expected deviation from their equilibrium state. The temperature at the crucible bottom was kept 2–3 °C higher than at the melt "mirror," in order to avoid spontaneous nucleation at the bottom.

## $YAI_3(BO_3)_4$

Figure 1 illustrates triangular cross sections at 20 wt.% YAB (Fig. 1b) and 17 wt.% YAB (Fig. 1c) of the YAB-( $K_2Mo_3O_{10}$ - $Y_2O_3$ - $B_2O_3$ ) system as projections of all solid phases crystallizing within the interval from 1150 °C to 900 °C during cooling process for the complex flux compositions represented on these triangles. Therefore, flux compositions denoted as field 1 on Fig. 1b, c can be considered for YAB single crystal growth by using the SGDS method.



**Fig. 1** Complex flux compositions for YAB crystal growth in the YAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>) pseudo-quaternary system: (**a**) a scheme of the triangular cross sections of its tetrahedron composition studied in this work; phase formations in the temperature range from 1150 °C to 900 °C for the triangles of complex flux compositions corresponding to 20 wt/% (**b**) and 17 wt.% (**c**) of YAB concentrations in the pseudo-quaternary phase diagram

Fig. 2 Schematic Η  $\Delta T = 2-3^{\circ}C$ representation of setup for experimental investigations of solubility and growth of RAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> crystals and a temperature profile along the 3 furnace axis: heating procedure (a) and crystal growth process (b) 1, Pt crucible: 2, SiO<sub>2</sub> or ceramic lid with a tube; 3, seed holder; 4,5, thermocouples £ Π 5 b а Т

It should be noted that the single-phase YAB crystallization (without other crystalline solids) is expanded substantially with a decrease in YAB concentration from 20 wt.% to 17 wt.%. The YAB saturation temperature decreases relatively with

increasing  $B_2O_3$  content in the fluxed melt. However, it is less affected by an increase in the K-trimolybdate concentration. Fluxed melts are quite different in their crystallization capabilities. For instance, if the solvent exceeds 15 wt.% of  $B_2O_3$ , spontaneous nucleation of crystals does not occur, although YAB crystals are nucleating upon impurity centers. An addition of yttrium oxide to the solvent leads to spontaneous nucleation of a number of YAB crystals, and their sizes are greatly increased. After an addition of potassium or lead fluorides to complex molybdate fluxes, the pseudo-quaternary system is transformed to a pseudo-five component YAB-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-KF(PbF<sub>2</sub>)-Y<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>) system. A lead additive (PbF<sub>2</sub> as a reducing agent) to potassium trimolybdate flux provides most optimal redox conditions, i. e., it impedes reducing Mo<sup>6+</sup> on the one hand and oxidation of Pb<sup>2+</sup> on the other. In other words, molybdenum in Mo<sup>5+</sup> form as well as lead atoms in oxidizing state can substitute a part of aluminum and/or rare-earth elements presented in the structure and, respectively, thereby, drastically deteriorate the quality of the crystals [26].

The temperature dependence of YAB solubility in the region studied is close to the linear one in c-T coordinates (Fig. 3a), and it differs greatly from the linear curve in lnc-1/T coordinates which being valid only for ideal solutions. The c-T solubility curves have bends usually in the regions near co-crystallizing phase boundaries.

Based on the above results, YAB single crystals were obtained by SGDS method using 130-150 ml platinum crucibles and a furnace construction similar to the experimental setup shown in Fig. 2. Since the quality of crystals grown under the same fluxed melt supersaturation is improved at higher temperatures, the higher flux concentration is more preferable. Mainly small "point" YAB seeds, measuring  $0.2 \times 0.2 \times 0.4$ – $0.5 \times 0.5 \times 1.5$  mm and fixed with a Pt wire of 0.10–0.15 mm in diameter, were usually used. Before SGDS process, the saturation temperatures of fluxed melts were also precisely confirmed by a probe technique. Then, a "point" YAB seed, overheated by 2-3 °C above the fluxed melt saturation temperature, was dipped into fluxed melt. In the run of crystal growth, supersaturation was kept by cooling down from 0.8 °C to 1.2 °C/day, following the experimental data on the solubility and crystallization kinetics. At the end of the run, the crystal was pulled out and cooled to the room temperature within several days (Fig. 3b, c). An addition of erbium and ytterbium (up to 1 and 10 wt.% at yttrium position, respectively, in YAB crystal structure) does not substantially effect on crystal growth conditions, and (Er,Yb):YAB crystals for eye-safe lasers can be successfully grown on the similar scheme.

Faceting of YAB crystals is represented by a small number of simple crystallographic forms, namely,  $\{11\overline{2}0\}$  and  $\{2\overline{11}0\}$  trigonal prisms and a rhombohedron  $\{10\\overline{1}1\}$  (Fig. 4a). Other faces, such as  $\{0001\}$ ,  $\{20\overline{2}1\}$   $\{02\overline{2}1\}$ , and  $\{40\overline{4}1\}$  have a "secondary" importance (Fig. 4b), and they appear rarely, depending on the crystal growth conditions. The habit elongation is connected with a nonstoichiometry of the K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub> solvent because of partial loss of potassium during long time of SGDS process [5], and this can lead to inclusions of Mo ions in reduced Mo<sup>5+</sup> form [26] up to 0.5 wt.% into the YAB crystal (Fig. 4c).



**Fig. 3** YAB crystallization: (a) YAB solubility (in wt.%) in multicomponent 89.5 wt.%  $K_2Mo_3O_{10}$ -10.5 wt.%  $B_2O_3$  (*1*) and 85.0 wt.%  $K_2Mo_3O_{10}$ -10.0 wt.%  $B_2O_3$ -5.0 wt.% KF (2) systems; (b) asgrown YAB crystals by SGDS method using 88.1 wt.%  $K_2Mo_3O_{10}$ -3.3 wt.%  $Y_2O_3$ -8.6 wt.%  $B_2O_3$  flux (initial YAB concentration 17 wt.%, growth temperature range from 1025 °C to 959 °C, cooling rate gradually increased from 0.8 °C to 1.2 °C/day); (c) the same both growth method and initial YAB concentration using 89.5 wt.% 5K\_2Mo\_3O\_{10}-10.5 wt.% B\_2O\_3flux (growth temperature range from 1027 °C to 875 °C, cooling rate from 0.8 °C to 1.2 °C/day); 1 mm scale

## GdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>

GdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (GdAB) field of single-phase crystallization in the GdAB-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-Gd<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>) system is restricted by B<sub>2</sub>O<sub>3</sub> and Gd<sub>2</sub>O<sub>3</sub> concentrations in the complex flux from 25 to 85 mol.% and 12–25 mol.%, respectively (Fig. 5a) [25]. At a much lower B<sub>2</sub>O<sub>3</sub> content, Al<sub>5</sub>BO<sub>9</sub> crystallizes together with GdAB at higher concentrations, and the fluxed melt segregates into layers. The maximum solubility of Gd<sub>2</sub>O<sub>3</sub> in this field is achieved for a B<sub>2</sub>O<sub>3</sub> content in the fluxed melt that varies from 25 to 30 mol.%. Increasing Gd<sub>2</sub>O<sub>3</sub> concentration over 25 mol.% leads to GdAB and GdBO<sub>3</sub> co-crystallization. In the range from 15 to 20 wt.% GdAB, its solubility curve is practically linear in C-T coordinates (Fig. 5b) [27]. On the whole, GdAB solubility is strongly dependent on the flux composition (Fig. 6a). Basing on these phase diagrams, GdAB single crystals were also grown on the scheme described above for YAl-borate (Fig. 7).

### $ErAl_3(BO_3)_4$

 $ErAl_3(BO_3)_4$  (ErAB) field of primary crystallization in the  $ErAl_3(BO_3)_4$ -( $K_2Mo_3O_{10}$ - $Er_2O_3$ - $B_2O_3$ ) system is in many respects similar to its YAB analogue



**Fig. 4** YAB crystal morphology: (a) most typical crystallographic forms; (b) a full-faceting crystal; (c) the influence of flux composition on the YAB crystal habit in dependence of the molybdenum content in YAB crystals versus the  $MoO_3$  concentration in the solvent

in a temperature range 900–1050 °C. ErAB single-phase field decreases sharply with increasing  $Er_2O_3$  concentration in the flux component, and it is replaced by crystallization of a high-temperature  $ErBO_3$  phase [27]. As for non-containing  $Er_2O_3$  fluxes, ErAB solubility curves are also similar to those in YAB-based fluxed melts, and the temperature coefficient of their solubility increases gradually with increasing  $Er_2O_3$  content in the system (Fig. 8) [28]. So, it is possible to grow ErAB single crystals from low-concentrated fluxed melts (7.0 mol.% or less). Further decrease in the ErAB concentration results in the replacement of the region of its solid phase stability by  $KEr(MoO_4)_2$  crystallization. ErAB solids were also grown from a potassium trimolybdate-based fluxed melt on small seeds using 130–150 ml platinum crucibles (Fig. 9).



**Fig. 5** GdAB-based phase diagram: (a) phase relationships and flux compositions for single-phase GdAB crystallization in the GdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-Gd<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>) pseudo-quaternary system within the temperature cooling interval 1150–900 °C (composition tetrahedron cross section for 20 wt.% GdAB concentration): *1*, homogenous melt; *2*, separation of fluxed melt; *3*, GdAB; *4*, GdAB+GdBO<sub>3</sub>; *5*, GdAB+Al<sub>5</sub>BO<sub>9</sub> (On the data of [25]); (b) GdAB solubility in the 83.1 wt.% K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-9.5 wt.% Gd<sub>2</sub>O<sub>3</sub>-7.4 wt.% B<sub>2</sub>O<sub>3</sub> (this is adequate to 54.6 mol.%K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-9.0 mol.% Gd<sub>2</sub>O<sub>3</sub>-36.4 mol.%B<sub>2</sub>O<sub>3</sub>) flux (On the data of [26])

### YbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>

No YbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (YbAB) single-phase crystallization was found in the pseudoquaternary 20 wt.% YbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-80 wt.% (K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Yb<sub>2</sub>O<sub>3</sub>) system in the temperature range of 1150–1050 °C. YbAB and YbBO<sub>3</sub> orthoborates co-crystallize in region 2 (Fig. 10a) [29]. Only small platelike hexagonal YbBO<sub>3</sub> crystals (1–2 mm in size) and needle-shaped Al<sub>5</sub>BO<sub>9</sub> ortho-tri-borate (5–6 mm long) were observed in regions 3 and 4, respectively.

As for the 15 wt.% YbAB cross section of the above complex system, singlephase YbAB formation was revealed under lowering temperature from 1100 °C to 1000 °C. Its field is limited by variations of the Yb<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> content in the flux from 5 to 10 mol.% and 20–40 mol.%, respectively (Fig. 10b). The 2–4 mm crystals of the YbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> were found on the walls and bottom of the crucibles in region *1*. These isometric YbAB crystals exhibit well-developed {1011}, {1120}, and {2110} faces.

In this case, the saturation points of YbAB insignificantly increase with an excess of ytterbium oxide in the complex  $K_2Mo_3O_{10}$ - $B_2O_3$ - $Yb_2O_3$  flux (Fig. 11a). On the other hand, these temperatures decrease substantially with increasing  $B_2O_3$  concentration in the  $K_2Mo_3O_{10}$ - $B_2O_3$  flux (Fig. 11b). Only YbBO<sub>3</sub> orthoborate crystallizes in region 3 (Fig. 10b), but increase in Yb<sub>2</sub>O<sub>3</sub> content up to 20 mol.% in the solvent leads to a considerable increase in the melting point of starting mixture (see Fig. 10, region 5).

In this way, as it can be seen from Fig. 11a, the YbAB solubility decreases with an addition of ytterbium oxide to the complex flux. On the whole, the absolute values of



Fig. 7 As-grown GdAB single crystal using the  $K_2Mo_3O_{10}$ -9.5 wt.% Gd<sub>2</sub>O<sub>3</sub>-7.4 wt.% B<sub>2</sub>O<sub>3</sub> complex flux (initial GdAB concentration 17 wt.%, growth temperature range from 1057 °C to 998 °C, cooling rate from 0.8 °C to 1.8 °C/day); 1 mm scale





YbAl-borate solubility are substantially higher in the complex flux containing 55 mol.%  $K_2Mo_3O_{10}$  and 45 mol.%  $B_2O_3$  than for its 55 mol.%  $K_2Mo_3O_{10}$ -40 mol.%  $B_2O_3$ -5 mol.%  $Yb_2O_3$  composition (Fig. 12a), and temperature coefficient of YbAB solubility also increases in the first case. The results obtained were used for growth of YbAB single crystals on "point" seeds by SGDS technique (Fig. 12b).

## Er:Yb<sub>x</sub>Gd<sub>1-x</sub>Al<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>

Difference in the nature of Yb and Gd cations realizes in the field width of primary GdAB and YbAB crystallization [25, 29]. Nevertheless, the phase relationships in the systems studied are similar to each other. The regions of single-phase YbAB and GdAB crystallization coincide in a comparatively narrow range. They somewhat overlap one another on the composition cross section at 900 °C as the projection of



100 mol.% K2M03O10

100 mol.% Yb,O,

**Fig. 10** Phase relationships in the systems 20 wt.% YbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-80 wt.% (K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Yb<sub>2</sub>O<sub>3</sub>) (**a**) and 15 wt.% YbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-85 wt.% (K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Yb<sub>2</sub>O<sub>3</sub>) (**b**) in the temperature range of 1150–1000 °C: (1) •, YbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>; (2), YbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> + YbBO<sub>3</sub>; (3) ▼, YbBO<sub>3</sub>; (4) ◆, Al<sub>5</sub>BO<sub>9</sub>; (5), partial melting + YbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, x does not melt at 1150 °C; (6), glass-forming melt; (7) ■, separating melt [29]

spontaneous *R*AB crystallization in the temperature interval from 1150 °C to 900 °C (Fig. 13). *R*AB concentration in the complex  $K_2Mo_3O_{10}$ - $B_2O_3$ - $R_2O_3$  flux for growth of co-doped (Er,Yb):GdAB single crystals seems to be not higher than 15–17 mol%.



The spontaneous (Er,Yb):GdAB crystals were obtained in the runs of experiments on phase relationships in the systems studied. They are colorless or have the characteristic erbium light pink color depending on Er concentration and of good optical quality (Fig. 14). All crystals are characterized by well-developed trigonal prisms  $\{11\overline{2}0\}$  and  $\{2\overline{11}0\}$  and rhombohedron  $\{10\overline{1}1\}$  faces. It is important to note



**Fig. 12** YbAB solubility in complex fluxes:  $I-55 \text{ mol.}\% \text{ K}_2\text{Mo}_3\text{O}_{10}$ -45 mol.% B<sub>2</sub>O<sub>3</sub>;  $2-55.0 \text{ mol.}\% \text{ K}_2\text{Mo}_3\text{O}_{10}$ -40 mol.% B<sub>2</sub>O<sub>3</sub>-5 mol.% Yb<sub>2</sub>O<sub>3</sub> (**a**) [29] and as-grown YbAB crystal (initial YbAB concentration 12 mol.%; initial complex flux composition 55 mol.% K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-40 mol.% B<sub>2</sub>O<sub>3</sub>-5 mol.% Yb<sub>2</sub>O<sub>3</sub>; growth temperature range 988–925 °C; cooling rate from 0.8 °C to 1.2 °C/day); 1 mm scale (**b**) [30]



that their habit extremely depends on the Gd<sub>2</sub>O<sub>3</sub> concentration in complex  $K_2Mo_3O_{10}-B_2O_3-R_2O_3$  flux composition, despite of the similar other growth conditions: elongated (Er,Yb):GdAB crystals were grown using  $K_2Mo_3O_{10}-B_2O_3$  solvent, but isometric crystals are formed in the Er:(Yb,Gd)Al<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>- $K_2Mo_3O_{10}-B_2O_3$ -(Gd,Er,Yb)<sub>2</sub>O<sub>3</sub> system. Then, these crystals were used as seeds for SGDS method.

Since the regions of (Er,Yb):GdAB single-phase crystallization do not exist at its concentration above 20 wt.% in the temperature range of 1150–900 °C, these crystals can be grown only at lower nutrient concentrations. From the viewpoint of the results obtained, a reasonable base for the growth of erbium and ytterbium co-



**Fig. 14** As-grown spontaneous GdAB crystals: (a) solvent  $K_2Mo_3O_{10}-B_2O_3-Gd_2O_3$ , (b) solvent  $K_2Mo_3O_{10}$ -B<sub>2</sub>O<sub>3</sub> (the background scale square corresponds to 1  $\times$  1 mm)



doped GdAB crystals seems to be the following pseudo-quaternary systems: 17 wt. % Er:(Yb,Gd)Al<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-83 wt.% (K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-(Gd,Er,Yb)<sub>2</sub>O<sub>3</sub>) with the flux compositions of 55 mol. % K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-45 mol. % B<sub>2</sub>O<sub>3</sub> (I) and 55 mol. % K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-40 mol. %B<sub>2</sub>O<sub>3</sub>-5 mol. % (Gd,Er,Yb)<sub>2</sub>O<sub>3</sub> (II).

Additions of ytterbium up to 15 wt.% to the GdAB nutrient in fluxed melt lead to increasing its solubility and, respectively, decreasing in the saturation temperature of high-temperature solutions: about 10-15 °C, depending on the flux composition (Fig. 15).

As a result, (Er,Yb):GdAB single crystals with optical quality and size up to  $20 \times 10 \times 10$  mm were grown on the seeds (Fig. 16). The above information on spontaneous crystal habits is useful for controlling the shape of the crystals grown from seeds, in order to minimize defects affecting the region near/around the "point" seed.

It has been found that the segregation coefficients  $K_s$  of rare-earth  $\mathrm{Er}^{3+}$  and  $\mathrm{Yb}^{3+}$ cations vary from 0.5 to 1.05 in as-grown (Er,Yb):GdAB crystals (Table 3). The main reason for such variation is the substantial difference in these  $R^{3+}$  cation sizes. In the case of (Er,Yb):YAB samples, these values are close to unity for both

 $R_2O_3$  systems



Fig. 16 (Er,Yb):GdAB crystals grown by SGDS method

admixtures as a consequence of the minor difference in the sizes of  $Y^{3+}$ ,  $Er^{3+}$ , and  $Yb^{3+}$  cations. The relatively higher values of  $K_s$  for ytterbium in run numbers 2105–2107 are most likely due to the increasing cooling rates (and therefore, increasing crystal growth rates) of the fluxed melts during spontaneous crystallization.

## LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>

At the first stage, phase formation in the complex LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-Lu<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>) system should be logically studied by using techniques and taking into account features of phase formation in the above-described multicomponent systems, namely, YAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>), GdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>), GdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Yb<sub>2</sub>O<sub>3</sub>), and (Er,Yb,Gd)Al<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Yb<sub>2</sub>O<sub>3</sub>) [21].

In the LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Lu<sub>2</sub>O<sub>3</sub> system, the sequence of solid phase nucleation upon cooling in the 1130-900 °C range depends on the flux composition. Crystallochemical feature of the lutetium in comparison with other rare-earth metals leads to significant differences in its crystal growth conditions. LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (LuAB) single-phase crystallization does not exist at a solute concentration less than 20 wt.% in the temperature range 1130–900 °C, while other RAB single crystals can be grown mostly in a relatively narrow region of solute content 15–20 wt.%. As it is shown in Fig. 17 for the 25 wt.% LuAB-75 wt.% ( $K_2Mo_3O_{10}$ -B<sub>2</sub>O<sub>3</sub>-Lu<sub>2</sub>O<sub>3</sub>) system, the LuBO<sub>3</sub> phase is formed in the cases of a Lu<sub>2</sub>O<sub>3</sub> excess and B<sub>2</sub>O<sub>3</sub> content of more than 30 mol.% in the flux. If the  $B_2O_3$  concentration is less than 30 mol.%, a cocrystallizing Al<sub>5</sub>BO<sub>9</sub> phase is formed. The LuAB single-phase crystallization field is relatively narrow in the given temperature range, as it is bounded by a thin dotted line in Fig. 17, and a bold dotted line indicates a wider area with a relatively equal proportions of co-crystallizing LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> and LuBO<sub>3</sub> solid phases. Increasing LuAB concentration up to 25 wt.% leads to mass spontaneous nucleation of these crystals. The size of isometric spontaneous LuAB crystals is about 1-2 mm, and they have a characteristic slightly brownish color. More homogeneous crystals are formed

Table 3	Microprobe analysis of (Er,Yb):GdA	B single crystals versus growth condi	tions: star	ting (T <sub>start</sub> )	and final (	T <sub>fin</sub> ) temperatu	re and run du	ration [32]
Borate c	omposition							
			$K_{s}$					
Run #	Dissolved in fluxed melt	As-grown crystal	Er	Yb	Gd	T <sub>start</sub> °C	T <sub>fin</sub> , °C	Durat., day
2074	$Er_{0.015}Yb_{0.11}Gd_{0.875}Al_3(BO_3)_4$	$Er_{0.01}Yb_{0.07}Gd_{0.92}Al_3(BO_3)_4$	0.67	0.64	1.05	1010	933	56
2104	$Er_{0.015}Yb_{0.11}Gd_{0.875}Al_3(BO_3)_4$	$\left  \ Er_{0.009} Yb_{0.07} Gd_{0.921} Al_3 (BO_3)_4 \right $	0.60	0.64	1.05	964	899	50
2105	$Yb_{0.01}Gd_{0.99}Al_3(BO_3)_4$	$Pb_{0.009}Gd_{0.991}Al_3(BO_3)_4$	I	0.90	1.00	1051	888	10
2106	$[Er_{0.008}Yb_{0.12}Gd_{0.872}Al_3(BO_3)_4$	${ m Er}_{0.004}{ m Yb}_{0.096}{ m Gd}_{0.90}{ m Al}_{3}({ m BO}_{3})_{4}$	0.50	0.80	1.03	1051	888	10
2107	$[Er_{0.015}Yb_{0.20}Gd_{0.785}Al_3(BO_3)_4$	$[Er_{0.012}Yb_{0.21}Gd_{0.778}Al_3(BO_3)_4$	0.80	1.05	0.99	1051	888	10

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**Fig. 17** Phase formation in the 25 mol.% LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-75 mol.% (K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-Lu<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>) fluxed melt within 1130–900 °C: K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Lu<sub>2</sub>O<sub>3</sub> flux compositions for spontaneous nucleation of various solids ( $\bigcirc$ , LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>; •, LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> + LuBO<sub>3</sub>; **□**, partial melting, i.e., initial mixture does not melt at 1130 °C during 24 h; x, Al<sub>5</sub>BO<sub>9</sub>) and regions for capability of crystalline phases to growth on seeds (*1*) overall LuAB stability field; (*2*) LuAB and LuBO<sub>3</sub> co-crystallization; (*3*) LuAB and Al<sub>5</sub>BO<sub>9</sub> co-crystallization

at 70 wt.%  $K_2Mo_3O_{10}$ , i.e., 30 wt.% LuAB. The crystals are rather transparent and their habit is typical for other *R*AB representatives. A decrease in the  $K_2Mo_3O_{10}$ /LuAB ratio (up 60/40 wt.%) does not change the size and shape of spontaneous LuAB crystals, but the crystal yield is decreased.

The color of grown crystals is varied from light brown to a substantially colorless, depending on the Lu<sub>2</sub>O<sub>3</sub> concentration in the fluxed melt, and LuAB crystals have rather high quality and transparency. Their faceting is characterized by two well-developed  $\{11\overline{2}0\}$  and  $\{2\overline{110}\}$  trigonal prisms and  $\{10\overline{11}\}$  rhombohedron faces. It should be noted that LuAB crystal habit and their color depend on the Lu<sub>2</sub>O<sub>3</sub> concentration in the K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Lu<sub>2</sub>O<sub>3</sub> system. Isometric brownish LuAB crystals were grown from LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Lu<sub>2</sub>O<sub>3</sub>) fluxed melt, but elongated transparent crystals were formed in the LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>) system. This result on morphological features of spontaneous LuAB crystals can be useful for controlling the crystal shape in SGDS process, in order to minimize defects affecting the region near/around the "point" seed.

The X-ray powder diffraction data of the LuAB crystals display their similarity with the ICDD structural data of other borates of huntite-type family, for example, HoAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (Fig. 18a). The LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> peaks are comparable with those for GdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> as well, although they are a bit offset from each other, but both pictures are similar on the whole. According to single crystal X-ray investigations, the LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> crystals obtained have the following unit cell parameters: a = 9.284 (10) Å, c = 7.211 (7) Å, V = 538(1) Å<sup>3</sup>, and R32 space group. Differential thermal







**Fig. 19** Replacement of the LuAB crystals by the LuBO<sub>3</sub> phase: (**a**) partial replacement; (**b**) almost complete replacement; (*1*) LuAB, (*2*) LuBO<sub>3</sub>

analysis (DTA) and XRD data show that LuAB is melted incongruently, similar to other rare-earth aluminum borates. The decomposition temperature is 1300 °C for the (Er,Yb):LuAB sample (Fig. 18b). LuAB samples begin to dissociate slowly at temperatures above 900 °C in ambient atmosphere, as it was shown for *R*AB single crystals, which is also characteristic of these borates [31]. A weak peak at 1340 °C can be responsible for LuBO<sub>3</sub> inclusions in the investigated phase. The powder XRD investigations of DTA-resulted products demonstrate high-temperature LuBO<sub>3</sub> phase with vaterite-type structure (*P*6<sub>3</sub>/mmc) and Al<sub>5</sub>BO<sub>9</sub> with their ratio of 24/76 in wt.%.

Complex K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-Lu<sub>2</sub>O<sub>3</sub> flux composition looks acceptable for slightly doped LuAB crystals. For example, in the case of earlier studied (Er,Yb,Gd) Al<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-B<sub>2</sub>O<sub>3</sub>-(Gd,Er,Yb)<sub>2</sub>O<sub>3</sub>) system [32], additions of ytterbium up to 15 wt.% to the GdAB nutrient in fluxed melt lead to an increase in its solubility and, respectively, to a decrease in the saturation temperature of high-temperature solutions: about 10–15 °C, depending on the flux composition. In the meantime, in the LuAB-based similar system, initial LuAB seed crystals are replaced by microcrystals of LuBO<sub>3</sub> trigonal modification (a = 4.92(2) Å, c = 16.17(16) Å, V = 340(4) Å<sup>3</sup>), as more high-temperature phase, at temperatures even higher than the LuAB saturation point (Fig. 19a). This leads to complete replacement of the LuAB seed crystal by LuBO<sub>3</sub> co-crystallizing phase and, as a result, to blockage of LuAB crystal growth interface (Fig. 19b).

The polymorphs of rare-earth borates  $RBO_3$ -type formation are defined by the cation sizes ratio in the structure ( $R^{3+}/O^{2-}$ ). For the lutetium, which one the smallest of the rare earth cation, this value is 0.607, the vaterite-type structure is stable above 1310 °C; the calcite-type structure is stable below this temperature [33]. The X-ray and composition studies of LuAB and LuBO<sub>3</sub> single crystals show the full compliance with the theoretical spectra for these compounds (Figs. 20 and 21). In this connection, the weak peak shown in Fig. 14b can be assigned to the structural



Fig. 20 XRD pattern (a), SEM image (b), and energy dispersion spectrum of an (Er,Yb):LuAB crystal (c)

transition in LuBO<sub>3</sub> as trace inclusions of this subsidiary phase into LuAB spontaneous crystals.

This behavior suggests crystallization of LuBO<sub>3</sub> primary phase over the wide range of the solvent composition (see Fig. 17). At certain concentrations, precipitated microcrystals LuBO<sub>3</sub> serve as seeds for the further growth of these LuAB. This fact is indirectly confirmed by a large number of small LuAB crystals during spontaneous growth. However, the XRD phase analysis does not provide information about the presence of foreign inclusions in LuAB because of too small content of this admixture.

Thus, it can be assumed that during cooling process,  $LuBO_3$  phase first crystallizes, and these microcrystals become substrates for LuAB crystal growth, i.e.,  $LuBO_3$  crystallizes as a primary phase in the entire region of stable LuAB crystallization (field 2 in Fig. 17). Therefore, its stability field is much wider in comparison with LuAB. According to the Le Chatelier's rule, adding the  $Al_2O_3$  amount up to



**Fig. 21** XRD pattern (**a**), SEM image (**b**), and energy dispersion spectrum of an (Er,Yb):LuBO<sub>3</sub> crystal (**c**)

30 wt.% into the initial melt of field 2 compositions leads to reducing the intensity of the LuBO<sub>3</sub> formation on a LuAB seed. However, an access of Al<sub>2</sub>O<sub>3</sub> significantly increases fluxed melt saturation temperature. In this case, Al<sub>5</sub>BO<sub>9</sub> is not found in solid-field high-temperature solution. A "point" seed of LuAB crystal is slowly destructed down, and it is covered by LuBO<sub>3</sub> microcrystals, even if temperatures slightly exceeded the LuAB saturation point (Fig. 22a), i.e., LuBO<sub>3</sub> microcrystals blocked the LuAB growing face (Fig. 22b). It should be noted that the LuBO<sub>3</sub> microcrystals are formed exclusively on the {1120} and {2110} faces, but it happens never on the {1011} rhombohedron. Thus, usage of [1011]-oriented LuAB crystal seed will probably allow to avoid formation of the external phase inclusions in its crystal growth process. On the whole, SGDS of LuAB single crystals (without LuBO<sub>3</sub>) is possible only in a narrow flux composition range (Fig. 17, region 3).

Taking into account the fact that an  $Al_2O_3$  addition into the  $K_2Mo_3O_{10}$ based complex flux gives optimistic results, it was decided to investigate phase



**Fig. 22** Formation of LuBO<sub>3</sub> microcrystals on LuAB trigonal prism faces (**a**), LuBO<sub>3</sub> microcrystals trapped and covered by growth layers of LuAB prismatic face (**b**)



**Fig. 23** Habit transformation of LuAB spontaneous crystals depending on the  $B_2O_3$  concentration in the complex flux  $K_2Mo_3O_{10}$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>: (a) 35 mol.%  $B_2O_3$ ; (b) 50 mol.%  $B_2O_3$ 

relationships in the LuAB-( $K_2Mo_3O_{10}-Al_2O_3-B_2O_3$ ) pseudo-quaternary system, emphasizing on comparison of phase relationships in this system and in the LuAB-( $K_2Mo_3O_{10}-Lu_2O_3-B_2O_3$ ) pseudo-quaternary system for SGDS method of improved LuAB single crystals as a solid-state matrix for Yb<sup>3+</sup> and Er<sup>3+</sup> dopants to be used in laser systems operating in near-infrared (NIR) spectral range.

Firstly, spontaneous crystallization of LuAB was investigated for initial borate concentrations from 15 to 40 wt.% in the LuAB-K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub> system. LuAB crystals are not formed if this component is 20 wt.% or less in the starting mixture. The size of isometric spontaneous LuAB crystals was about 1–2 mm, and sometime they have a characteristic slightly brownish color (Fig. 23a). LuAB crystals are rather transparent and their habit is typical for other *R*AB representatives. Faceting all of them is characterized by two well-developed {11 $\overline{2}$ 0} and {2 $\overline{11}$ 0} trigonal prisms and rhombohedron {10 $\overline{11}$ } faces. It should be noted that the habit of the crystals obtained is largely determined by the ratio of the complex flux components: in the case the



**Fig. 24** Phase formation in the 25 mol.% LuAB-75 mol.% ( $K_2Mo_3O_{10}-Al_2O_3-B_2O_3$ ) fluxed melt within 1130–900 °C:  $K_2Mo_3O_{10}-B_2O_3-Lu_2O_3$  flux compositions for spontaneous nucleation of various solids

 $B_2O_3$  concentration increases, the habit of crystals transforms from isometric to elongated (Fig. 23b) and the faces of the rhombohedron becoming less until they completely disappear.

The low-temperature LuBO<sub>3</sub> crystallizes as a primary phase in the entire region of stable crystallization of the LuAB. Adding the  $Al_2O_3$  up to 25 wt.% into the initial melt compositions leads to strong reducing the intensity of the LuBO<sub>3</sub> formation. This access of  $Al_2O_3$  does not lead to great increasing fluxed melt saturation temperature.

In the LuAB-(K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>) system, the sequence of solid phase nucleation upon cooling in the 1130–900 °C range depends on the flux composition. The LuAB single-phase crystallization field is relatively narrow in the given temperature range (Fig. 24), but the region bounded by a thin dotted line indicates a wider area with mainly LuAB phase crystallization (including small amount of co-crystallized Al<sub>5</sub>BO<sub>9</sub> and vaterite-type LuBO<sub>3</sub> phase). Decreasing B<sub>2</sub>O<sub>3</sub> concentration in the complex flux leads to a gradual decrease in the amount of LuAB and causes formation of parasitic Al<sub>5</sub>BO<sub>9</sub> and LuBO<sub>3</sub> phases. Further decrease in the amount of B<sub>2</sub>O<sub>3</sub> (less than 10 mol.%) promotes only Al<sub>5</sub>BO<sub>9</sub> crystallization. An increase in the Al<sub>2</sub>O<sub>3</sub> amount in the flux also leads to a gradual dominance of Al<sub>5</sub>BO<sub>9</sub> and LuBO<sub>3</sub> phases in the final product, before melting temperature of the starting mixture is not higher 1130 °C.



**Fig. 25** As-grown LuAB single crystals by using SGDS method: (a)  $60 \text{ mol.}\% \text{ K}_2\text{Mo}_3\text{O}_{10}$ -30 mol. % B<sub>2</sub>O<sub>3</sub>-10 mol.% Al<sub>2</sub>O<sub>3</sub> complex flux; (b) 50 mol.% K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-40 mol.% B<sub>2</sub>O<sub>3</sub>-10 mol.% Al<sub>2</sub>O<sub>3</sub> complex flux

On the whole, the results obtained allow to grow LuAB single crystals by SGDS method basing on the phase diagram studied. Taking this fact into account, (Er,Yb): LuAB crystal growth conditions were refined using  $K_2Mo_3O_{10}$ -B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> complex flux. (Er,Yb):LuAB single crystals exceeding 10 mm in size for optical measurements were grown during a month within 40 °C cooling interval (Fig. 25). The most preferable flux compositions within the "dotted line" are shown in Fig. 24.

#### (Er,Yb):YAB Crystalline Thin Layers

Among the waveguide fabrication methods, liquid phase epitaxy (LPE) was found to be a reliable, simple, and low-cost technique, allowing to produce the waveguides with low propagation losses and high crystalline quality. As for the *R*AB, LPE growth is solely a suitable technique for preparation of single crystalline layers because of incongruent melting of *R*Al-borates. The (Er,Yb):YAB layers were recently tested as passive optical waveguides [34]. Spectroscopic investigations have shown good crystallinity of the obtained layers. The propagation losses have been measured to be approximately 2 dB/cm in the 50  $\mu$ m thick (Er,Yb):YAB waveguide. This value is quite high for LPE grown by this method. So, further experiments were performed for optimization of (Er,Yb):YAB layer growth technology [35–37].

Single crystal layers of Yb:YAB, Er:YAB, and (Er,Yb):YAB were grown on YAB substrates of different orientations, prismatic and rhombohedral [36, 37]. The substrate material should approximately match the material to be deposited both in lattice parameters and in linear thermal expansion coefficients. In this respect, single crystals of YAB seem to be the optimum substrates for the LPE of *R*:YAB (R=Er, Yb) layers because misfit of the cell parameters between YAB substrate and *R*:YAB layers is small (Fig. 26). This adaptation of the crystallographic structures of both materials can avoid dislocations and stacking faults. Furthermore, differences in



**Fig. 26** Cell parameters a (a) and c (b) of YAB (1) and Yb:YAB (2) crystals versus temperature [35]

**Table 4** Linear thermal expansion coefficients ( $\alpha$ ) of YAB and (Er,Yb):YAB solids along [100] direction [36]

Compound	$\alpha_{[100]}, 10^{-6} \text{ K}^{-1}$	$\alpha_{[001]}, 10^{-6} \text{ K}^{-1}$
YAl <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	4.2	12.97
Er <sub>0.015</sub> Yb <sub>0.11</sub> Y <sub>0.875</sub> Al <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>	4.4	13.17

refractive indices between the substrate and the active layer are principle as YAB crystalline thin layers doped with  $Er^{3+}$  and  $Yb^{3+}$  are very attractive for applications in active waveguide devices, such as planar and channel waveguide lasers. While homoepitaxy obviously leads to excellent lattice and symmetry matching and with identical melting temperatures, thermal expansion coefficients, composition, etc., it is not helpful as a method of making waveguides as the film needs to have a different refractive index to the substrate. The refractive index of the film must be higher than that of the substrates to enable a guiding in this case. According to [38], replacement of  $Y^{3+}$  by  $Yb^{3+}$  up to 7 wt.% results in an increase of ordinary and extraordinary refraction indices by ~0.002 and 0.001, respectively. In this respect, single crystals of YAB seem to be the optimum substrate for the LPE of (Er, Yb):YAB layers. The presence of a small amount of dopant cations does not change the development of the layers, so the LPE growth can be considered as almost homoepitaxial. Also, doping insignificantly affects the thermal expansion coefficients (Table 4).

Single crystals of YAB for substrate preparation were obtained by SGDS method basing on their solubility diagrams (see Fig. 3). YAB crystalline substances in the starting solutions were 17 wt.%. Before SGDS, the saturation temperatures of fluxed melts were precisely determined by a probe technique, and it was found to be 1060–1080 °C depending on the dopant concentration. A "point" YAB seed of  $0.3 \times 0.3 \times 1.0$  mm dimension was dipped into fluxed melt. During the crystal growth, supersaturation was kept within the temperature interval of 1080–1000 °C by the cooling of fluxed melts in the range of 0.2-5 °C/day following the

experimental data on the solubility and crystallization kinetics. At the end of growth process, the crystal was pulled out and cooled to the room temperature within several days (Fig. 27). Substrate wafers with sizes up to 7–10 mm and thickness of 0.5–1.5 mm were cut from undoped SGDS-grown YAB single crystals parallel to  $\{10\overline{1}1\}$  and  $\{11\overline{2}0\}$  or  $\{2\overline{11}0\}$  planes.

The thin film growth was performed under similar conditions. At the beginning of epitaxial growth, the YAB substrate was slowly dipped into the solution at temperature 1–2 °C higher than saturation point ( $T_{sat}$ ). Ten to 20 min later, the temperature was lowered to 3–12 °C below  $T_{sat}$  for film crystallization process under static conditions or with rotation at 5.5 rpm. LPE procedure was varied from 2 to 36 h, depending on supercooling of the fluxed melt and on expected thickness of the layer, as it follows from their growth kinetics. Finally, the substrate and film grown were pulled out slowly, cooled to the room temperature, and released from the residual crystallized melt by sequential dissolution in hydrochloric acid, distilled water, and ethanol, step-by-step.

As it follows from the data obtained, normal growth rates of epitaxial layers are similar for all investigated R:YAB layers. Figure 28a shows the thickness of Yb: YAB films grown on YAB substrate wafers cut parallel to  $\{10\overline{1}1\}$  plane versus the growth time. The growth rate (V) of the layers was determined to be within the range of 0.07–0.35  $\mu$ m/min for the interval of fluxed melt supercooling ( $\Delta$ T) from 5 °C to 20 °C (Table 5, Fig. 28b). These values are from one-third to one-fifteenth as large in comparison with the growth rate of the NdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> layers obtained from PbO-PbF<sub>2</sub> flux system by the authors of [39], but they are comparable with the results of [27,36] for molybdate-based LPE. On the other hand, these data also agree with kinetic growth of YAB bulk crystals from K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>-based high-temperature solutions [40]. In this case, the normal growth rate of Yb:YAB films is also characterized on the whole by linear dependence on supercooling (supersaturation) of the fluxed melt (Fig. 28b). It implies the similar and high level of the growth activation energy, as a result of substantial restrictions to transport BO<sub>3</sub> groups from the polymerized melt to an isolated state at the solid-liquid phase boundary. It was found that Yb concentration in grown films slightly increases from 0.09 to 0.11 with an increase of supercooling/supersaturation (Table 5).

The growth rate of (Er,Yb):YAB and Er:YAB single crystal layers was estimated to be within the range of 0.017–0.31  $\mu$ m/min (Fig. 29) [36]. The average Er and Yb effective distribution coefficient is 0.84 as a consequence of minor differences in the sizes of Y<sup>3+</sup>, Er<sup>3+</sup>, and Yb<sup>3+</sup> cations.

Microrelief of as-grown Yb:YAB films depends on the growth conditions and substrate orientation (Fig. 30). Formation of growth hillocks is typical on corners and edges of the substrate, i.e., where the solution flow is enriched with solute material. Precise investigations show that edge nucleation can be dominant under higher supersaturations at the last stages, although growth mechanism of single crystal layers from fluxed melt has usually screw-dislocation nature. Besides growth spirals and vicinal hillocks, the characteristic features of most of the faces are cusps and corrugations, although flat areas are presented on the epitaxial layer surface. Thus, the substrate is considered as a rough surface with nucleation occurring



**Fig. 27** LPE of (Er,Yb):YAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> single crystal layers: (**a**) a furnace for SGDS and LPE techniques: (1) Al<sub>2</sub>O<sub>3</sub> crystal holder, (2) Al<sub>2</sub>O<sub>3</sub> ceramics, (3) thermocouple, (4) heater, (5) Pr crucible, (6) crystal seed/substrate, (7) fluxed melt; (**b**) as-grown YAB single crystals for LPE substrates; (**c**) a schematic representation of YAB crystallographic planes used for making sub-strates; (**d**) YAB substrate wafers cut parallel to (1011) plane [35]

randomly rather than at screw dislocations. The concentration of vicinal cusps is higher on crystal edges as a result of a higher local supersaturation. Corner and edge nucleation can be initiated by a relatively high concentration of fluxed melt in these regions. An increase in supersaturation leads to the rising cusp steepness. However, this mainly happens when layer growth becomes unstable. Thus, formations of



**Fig. 28** Dependence of the thickness (h) of Yb:YAB layers on the growth time ( $\tau$ ): (1)  $\Delta T = 5 \,^{\circ}$ C; (2)  $\Delta T = 10 \,^{\circ}$ C; (3)  $\Delta T = 20 \,^{\circ}$ C (**a**) and normal growth rate of Yb:YAB films versus supercooling of solution (**b**) [37]

Run number	ΔT, °C	t, min	Thickness, µm	V, µm/min	Composition of layers
47	5	120	8	0.07	Yb <sub>0.092</sub> Y <sub>0.908</sub> Al <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub>
48	5	240	16	0.07	$Yb_{0.093}Y_{0.907}Al_3(BO_3)_4$
50	10	120	22	0.18	$Yb_{0.106}Y_{0.894}Al_3(BO_3)_4$
51	10	240	44	0.18	$Yb_{0.104}Y_{0.896}Al_3(BO_3)_4$
53	20	120	42	0.35	$Yb_{0.110}Y_{0.890}Al_3(BO_3)_4$
54	20	240	84	035	$Yb_{0.105}Y_{0.895}Al_3(BO_3)_4$

 Table 5 Experimental results of Yb:YAB thin film growth [37]

growth hillocks, their quantitative and qualitative variations, to some extent, are the result of growth conditions.

The surface morphology of (Er,Yb):YAB layers is flat over large areas. No visible solution inclusions are observed in the layers. Though the polished edge looks optically qualitative, the as-grown surface has some imperfections and cracks. All the surface irregularities are less than 50 mm in size (Fig. 31a). The border between the doped film and the undoped substrate is clearly visible in the polarized light (Fig. 31b).

#### **RAB Glass-Ceramic Composites**

Since borate melts tend to glass formation, microcrystallization processes in  $RAl_3(BO_3)_4$ -B<sub>2</sub>O<sub>3</sub> (R=Y,Gd) systems were studied, to compare spectroscopic characteristics of Er and Yb co-doped YAB and GdAB single crystals and glass-ceramic materials with similar chemical composition [41]. This is one of the priorities on the way toward searching relatively low-cost optical glass-ceramic materials as alternative components of compact laser systems.



**Fig. 29** Normal growth rate of *R*:YAB epitaxial layers versus relative supercooling: *l*,  $Er_{0.015}Yb_{0.11}Y_{0.875}Al_3(BO_3)_4$ ; *2*,  $Er_{0.04}Y_{0.96}Al_3(BO_3)_4$  [36]



**Fig. 30** Typical relief of as-grown Yb:YAB films: (a) a layer parallel to  $(10\overline{1}1)$ ,  $\Delta T = 20$  °C,  $\tau = 4$  h; (b) a layer parallel to  $(11\overline{2}0)$ ,  $\Delta T = 20$  °C,  $\tau = 4$  h [37]

Starting YAB and GdAB compositions with an excess of boron oxide were first synthesized by solid-state reactions, i.e., they were annealed in a high-temperature muffle furnace with a 2.5 kW silicon carbide heater and then quenched (vitrified). Sequentially, pellets of the mixture of rare earth, boron, and aluminum oxides with diameter of 8 mm were prepared at the pressure of 4GPa, heated up to 1100 °C, grained, and re-heated again, in order to complete the solid-state reaction. The material obtained was mixed with the boron oxide as a glass-forming component, put into a specially shaped 10 ml Pt crucible, and completely melted. After several hours, needed to achieve complete homogenization of the melt, the mixture was quenched on a massive steel plate, covered by platinum foil to avoid the possible reaction with the melt.



Glass-ceramic materials based on the YAB and GdAB compounds in a wide temperature range differ in their characteristics. Opaque glass-ceramics (glaze) was obtained, when the starting mixture composition corresponded to the borate stoichiometry (Fig. 32a). In the case of 100 wt.% boric anhydride additive to the starting mixture, a transparent material was obtained (Fig. 32b). It was found that optimal temperature for the synthesis of YAB-based glass-ceramic composites is 1250 °C, and it corresponds 1350 °C for GdAB-based glass-ceramic composites.

The samples obtained are characterized by two types of X-ray diffraction patterns: typical patterns for amorphous material (blue lines) and patterns with welldefined reflections (red lines) indicating the presence of crystalline phase in a glassy matrix. As a rule, they coincide with X-ray spectra of GdAB and YAB crystals (Fig. 33).

Electron microscope images of YAB-containing glazes demonstrate cavities, most likely, associated with the removal of volatile components during crystallization process. According to microprobe analysis, there are areas of different composition in glass matrix that could also indicate the formation of nano-sized crystallites. Needlelike microcrystals are detected in transparent GdAB-based composites (Fig. 34a), while two types of microcrystals are found in the glaze: elongated, up to several microns, needles, with a ratio of length to width about 10/1 and idiomorphic prismatic small crystals (Fig. 34b).

**Fig. 31** 50  $\mu$ m thick asgrown (Er,Yb):YAB layer (**a**) and polarized optical image of the polished side facet of the same layer grown on the (101 1)-oriented YAB substrate (**b**) [40]



Fig. 32 As-obtained ceramics: (a) GdAB-containing glaze; (b) transparent YAB- and GdAB-based glass-ceramic composites [41]

X-ray microtomography method shows that crystalline phase content in a  $1 \times 1 \times 1$  mm volume of glass matrix is up to 32.5%, while the content of cavities corresponds to 0.35% (Fig. 35).

## Laser-Related Spectroscopy

#### Experimental

The absorption spectra of materials were measured at room temperature using Varian CARY-5000 spectrophotometer with spectral resolution of 0.3–2 nm. The luminescence intensity spectrum was measured with a setup shown in Fig. 36 [21]. A fiber-coupled laser diode emitting at 975 nm was used as an excitation source. The luminescence signal from the sample was collected on the enter slit of MDR-23 scanning monochromator with wide aperture lens. Hamamatsu InGaAs photodiode was used to register optical signal on the exit slit of the monochromator. Stanford Research Systems SR830 lock-in amplifier was utilized to increase the sensitivity and reduce influence of noises. For this reason the luminescence signal was modulated with a chopper connected to the amplifier.

The luminescence dynamics of all samples were measured at room temperature with optical parametrical oscillator pumped by the third harmonic of actively Q-switched Nd:YAG laser used as an excitation source. The pulse duration was about 20–30 ns. The luminescence radiation was forwarded to MDR-12 monochromator, and Hamamatsu InGaAs photodiode was mounted on its exit slit. The signal was observed and averaged on 500 MHz digital oscilloscope.

As for (Er,Yb):YAB layers testing as passive optical waveguides, the emission of a Ti:sapphire laser at 900 nm was focused by a microscope objective with a numerical aperture (NA) of 0.4 to the in coupling end-face of the waveguide. The waveguide orientation corresponded to light propagation along the







Fig. 34 Microcrystals in a glass matrix: (a) secondary electron image; (b) backscattered electron image of elongated and idiomorphic small crystals [41]



crystallographic c-axis. The outcoupled light was imaged onto the chip of a CCD (charge-coupled device) camera using another microscope objective.

## $(Er, Yb):YAI_3(BO_3)_4$

image for GdAB-based

volume [41]

Room temperature polarized absorption spectra of (Er,Yb):YAB crystal around 980 nm are shown in Fig. 37 [42]. A strong absorption band corresponding to  ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$  transition of Yb<sup>3+</sup> ions in (Er,Yb):YAB crystal is centered at 976 nm in  $\sigma$ -polarization, with a maximum absorption cross section of about  $2.75 \cdot 10^{-20}\,\text{cm}^2$ and a bandwidth of 17 nm (FWHM).



**Fig. 36** Setup for luminescence measurements: 1, the excitation source (a laser diode,  $\lambda = 975$  nm); 2, the sample; 3, the monochromator MDR-23; 4, the lock-in amplifier SR830; 5, the photodetector; 6, the control unit of the monochromator; 7, PC; 8, the chopper; 9, the lenses [21]



A number of local maxima are observed in the 1480–1605 nm range of (Er,Yb): YAB absorption spectra in both polarizations. The strongest maximum with cross section of about  $3.8 \cdot 10^{-20}$  cm<sup>2</sup> is located at 1530 nm in  $\sigma$ -polarization.

The luminescence decay time of  ${}^{4}I_{13/2}$  level was measured to be of about 325 µs. The measured lifetime is significantly shorter than that calculated from the Judd-Ofelt analysis (4.41 ms [43]). Thus the luminescence quantum efficiency for the  ${}^{4}I_{13/2}$  manifold of Er:YAB is of about 7%.

 $^2F_{5/2}$  energy level lifetime in Yb:YAB crystal was measured to be 480  $\pm$  5  $\mu s$ , whereas it is of about 60  $\pm$  5  $\mu s$  in (Er,Yb):YAB. The shortening of Yb^{3+} radiative lifetime in the erbium-ytterbium co-doped crystal in comparison with the ytterbium-doped one indicates a strong non-radiative energy transfer from Yb to Er ions. The energy transfer efficiency was obtained to be of about 88%.



## (Er,Yb):GdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>

The polarized absorption spectra of (Er,Yb):GdAB crystal around 980 nm at room temperature are similar to (Er,Yb):YAB spectra shown in Fig. 37. A strong absorption band corresponding to transition  ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$  of Yb<sup>3+</sup> ions is centered at 976 nm with a maximum absorption cross section of about 3.6  $\times 10^{-20}$  cm<sup>2</sup> and bandwidth of 18 nm (FWHM) in  $\sigma$ -polarization. Due to a comparatively broad absorption band, thermal control of the pump laser diode in laser experiments is not necessary.

Figure 38 shows room temperature polarized absorption spectra of (Er,Yb): GdAB in the 1450–1650 nm spectral range (transition  ${}^{4}I_{15/2} \rightarrow {}^{4}I_{13/2}$  of erbium ions). A number of local maxima are observed in both  $\sigma$ - and  $\pi$ -polarizations. The decay curve of 1.5 µm emission was single exponential, and luminescence decay time of  ${}^{4}I_{13/2}$  level was measured to be of about 350 µs. The measured lifetime is significantly shorter than that calculated from the Judd-Ofelt analysis (3.72 ms). Thus, the luminescence quantum efficiency for the  ${}^{4}I_{13/2}$  level of (Er,Yb):GdAB was estimated to be of about 10%. Such low quantum efficiency is similar to (Er,Yb): YAB (7% [44]) and explained by the large phonon energy in oxoborate crystals.

The lifetime of  ${}^{4}I_{11/2}$  level was estimated by measuring the rise time of luminescence from  ${}^{4}I_{13/2}$  in Er and Yb co-doped crystal pumped at 976 nm. The measured time was 2.4 µs, but it is considerably longer, than that obtained in Er single-doped YAB (80 ns [44]). It is explained by the fact that the presence of ytterbium ions leads to the increase of measured time due to energy back transfer.

The  ${}^{2}F_{5/2}$  level lifetimes of Yb<sup>3+</sup> were measured both in Yb single-doped crystal and in Er and Yb co-doped GdAB. To prevent reabsorption caused by significant overlap of the absorption and emission bands, all measurements were performed with fine powder of the crystals immersed in glycerin [45]. The lifetime of ytterbium ion in (Yb(0.8 at.%)):GdAB was measured to be 450 µs. The energy transfer efficiencies in (Er,Yb):GdAB are similar to those in (Er,Yb):YAB and Er and Yb

	Er <sup>3+</sup>	Yb <sup>3+</sup>			
	ions,	ions,	<sup>2</sup> F <sub>5/2,</sub> μs (Yb	<sup>2</sup> F <sub>5/2,</sub> μs (Yb,Er	Energy transfer
Crystal	at.%	at.%	single-doped)	co-doped)	efficiency, %
GdAB	1.0	8.0	450	75	83
	0.2	12		120	73
	1.2	22		38	92
YAB	1.5	8.4	480	47	90
	1.5	12	]	31	94

Table 6 Lifetimes of the  $^2F_{5/2}$  level of  $Yb^{3+}$  and energy transfer efficiencies in (Er,Yb):GdAB in comparison with (Er,Yb):YAB [32]



co-doped glass and more efficient than in vanadates and tungstates. Their values in comparison with (Er,Yb):YAB are shown in Table 6.

The stimulated emission cross-section spectra calculated by the integral reciprocity method are shown in Fig. 39. The highest stimulated emission cross section of about  $2.1 \times 10^{-20}$  cm<sup>2</sup> is located at 1531 nm.

## (Er,Yb):LuAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>

The unpolarized absorption cross-section spectrum of the (Er,Yb):LuAB crystal in the spectral range of 880–1060 nm  $({}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$  transition of ytterbium ions) contains a broad absorption band with maximum absorption cross section of  $1.1 \times 10^{-20}$  cm<sup>2</sup> near 980 nm, which coincides with the emission wavelengths of commercial InGaAs laser diodes (Fig. 40a). A number of local maxima are observed in room temperature unpolarized absorption spectra of (Er,Yb):LuAB crystal in the spectral range of 1470–1620 nm (transition  ${}^{4}I_{152} \rightarrow {}^{4}I_{132}$  of erbium ions), and the maximum absorption cross section of  $1.6 \times 10^{-20}$  cm<sup>2</sup> is located at 1485 nm (Fig. 40b).



Fig. 40 Room temperature absorption cross-section spectrum of an (Er,Yb):LuAB crystal: near  $1 \ \mu m$  (a); near 1.5  $\mu m$  (b) [21]

There is a peak with maximal intensity at 1522 nm on the measured luminescence spectrum of (Er,Yb):LuAB crystal (Fig. 41a). The decay curve of 1.5  $\mu$ m emission is single exponential, and the decay time is measured to be about 330  $\pm$  5  $\mu$ s (Fig. 41b).

#### (Er,Yb):YAB Crystalline Thin Layers

The room temperature absorption spectra of LPE-grown Er,Yb:YAB thin films in the 1 µm spectral region were compared with those of (Er,Yb):YAB bulk crystals [34].



Fig. 41 Room temperature luminescence spectrum of (Er,Yb):LuAB crystal near 1.5  $\mu$ m (a); luminescence decay curve of (Er,Yb):LuAB crystals near 1.5  $\mu$ m (b) [21]



**Fig. 42** Room temperature absorption spectra of (Er,Yb):YAB bulk crystal and LPE-grown film in  $\sigma$ -polarization (**a**) and room temperature fluorescence spectra of those for both polarizations (**b**) [34]

The results for  $\sigma$ -polarization are shown in Fig. 42a. The ytterbium  ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$  absorption band in the thin film has a full width at half maximum (FWHM) of 17 nm and is not broadened in comparison with the bulk crystal.

The room temperature 1.5  $\mu$ m emission spectra of the (Er,Yb):YAB bulk crystal and the thin film are plotted in Fig. 42b.The spectra of the crystal and

**Fig. 43** Near-field image of the outcoupled 900 nm light from the Er,Yb:YAB waveguide [34]



the thin film look very similar. The strongest fluorescence peak is located at the wavelength of 1531 nm for both polarizations.

For lifetime measurements the samples were excited by an optical parametric oscillator tuned to 976 nm with a pulse duration of 20 ns. The fluorescence decay curves of the Yb emission around 1  $\mu$ m and the Er emission around 1.5  $\mu$ m were measured by a photomultiplier behind a 0.5 m monochromator. The lifetimes of  ${}^{4}I_{13/2}$  energy level of Er and  ${}^{2}F_{5/2}$  energy level of Yb in the (Er,Yb):YAB bulk crystal and in the thin film were found to be 325  $\mu$ s (bulk) and 319  $\mu$ s (film) for the Er level and 60  $\mu$ s (bulk) and 50  $\mu$ s (film) for the Yb level. The similarity of the spectroscopic properties of the LPE-grown thin films and the (Er,Yb):YAB bulk crystals indicates a good film crystallinity.

The intensity distribution of the outcoupled emission of a Ti:sapphire laser from the sample end facet in passive waveguide tests is shown in Fig. 43. As expected for a 50  $\mu$ m thick film, several waveguide modes can be seen. The intensity of outcoupled fluorescence in horizontal direction is not uniform because of several defects inside the layer. Some background light is present in the substrate, due to ineffective coupling and waveguide losses. The excitation wavelength was tuned from 900 to 1000 nm, and the resulting fluorescence intensity at 1.5  $\mu$ m was detected using a Ge photodiode. The parasitic propagation losses were measured to be approximately 2 dB/cm in the 50  $\mu$ m thick (Er,Yb):YAB waveguide. This value is quite high for LPE-grown crystalline layers indicating that further optimization of layer growth technology is needed.

#### (Er,Yb):RAB Glass-Ceramic Composites

The absorption spectra of (Er,Yb):YAB-based glass-ceramic composites at 850–1050 nm and around 1500 nm are shown in Fig. 43. There is a wide absorption



band having a width of about 85 nm at 900–1000 nm with a high peak at 975 nm where absorption coefficient reaches 9.1 cm<sup>-1</sup>. This absorption band is composed by overlapped bands produced by both erbium  ${}^{4}I_{15/2}$ - ${}^{4}I_{11/2}$  and ytterbium  ${}^{2}F_{7/2}$ - ${}^{2}F_{5/2}$  transitions. However, considering higher doping level of Yb<sup>3+</sup> ions, their contribution to the absorption in this spectral range is anticipated to be significantly higher. The obtained absorption spectrum of the glass-ceramic composite is comparable with the spectra of Yb-doped functional phosphate glasses [46]. The spectrum at around 1500 nm is attributed to  ${}^{4}I_{15/2} \rightarrow {}^{4}I_{13/2}$  energy level transition of Er<sup>3+</sup> ions (Fig. 43b). There is a broad absorption band with full width at half maximum of 73 nm with peak of 0.25 cm<sup>-1</sup> at 1525 nm (Fig. 44).

The measured luminescence spectrum of (Er,Yb):YAB glass-ceramic composites has a smooth shape extending to 1700 nm with peak at 1525 nm and shoulders at around 1537 and 1550 nm [41]. The decay curve demonstrates an exponential decay with a time constant of 440  $\mu$ s, and it defines <sup>4</sup>I<sub>13/2</sub> energy level lifetime of Er<sup>3+</sup> ions.

Similar spectroscopic results were obtained in the case of (Er,Yb):GdAB glass-ceramic composites as well.

## **Concluding Remarks and Outlook**

From the spectroscopic point of view, the obtained results on SGDS technology of (Er,Yb):*R*AB single crystals and their solid solutions can be considered as a key base for development of highly efficient optical and compact diode-pumped laser systems operating in 1.5–1.6  $\mu$ m eye-safe spectral range. A major problem which awaits clarification concerns restrictions due to primary formation of some co-crystallizing phases in the *R*AB crystal growth process. In this connection, both mechanisms incongruent melting and incongruent dissolving in the most acceptable flux systems should be studied in detail for *R*Al-borates with device potential. In particular, optimization of (Er,Yb):*R*AB crystal growth technology is also actual for fabrication of (Er,Yb):*R*AB-based laser active elements.

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