

## STRUCTURAL AND LUMINESCENT PROPERTIES OF $\text{YAl}_3(\text{BO}_3)_4:\text{Ce}^{3+},\text{Tb}^{3+}$ POLYCRYSTALS SYNTHESIZED BY COLLOID CHEMICAL APPROACHES

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Polycrystalline phosphors of yttrium aluminum borates  $\text{YAl}_3(\text{BO}_3)_4$  activated with  $\text{Tb}^{3+}$  ions and co-activated with  $\text{Ce}^{3+}$  ions were synthesized by colloid chemical approaches: co-precipitation of hydroxides from corresponding salts aqueous solutions in the presence of boric acid with a subsequent heat treatment. Their phase composition, morphology and luminescence were investigated. The intensity of luminescence of the  $\text{Tb}^{3+}$  under UV excitation ( $\lambda_{\text{exc}} = 310 \text{ nm}$ ) is increased by two orders of magnitude for samples co-activated with  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  ions. That indicates the effective sensitization of  $\text{Tb}^{3+}$  luminescence by  $\text{Ce}^{3+}$  ions.

### 1. Introduction

Borates with the general formula  $\text{RM}_3(\text{BO}_3)_4$ , where R is rare earth ions or yttrium, M is Al, Fe, Ga, Cr form crystals with a huntite structure. They have pronounced fluorescent and nonlinear optical properties as well as high thermal, chemical and mechanical stability. In addition, they exhibit an abnormally low concentration quenching of the luminescence of lanthanide ions due to ion-ion excitations transfer related to the large minimum distance between the ions equal to 0.59 nm [1]. This is due to the structure of huntite in which  $[\text{RO}_6]$  polyhedra separated by  $[\text{BO}_3]$  ones.

Yttrium alumoborate ( $\text{YAl}_3(\text{BO}_3)_4$ , (YAB)) characterized by optical transparency over the wavelength range from 200 to 7000 nm is the most promising among borates. Luminescent materials with desired parameters could be obtained by replacing of  $\text{Y}^{3+}$  ions by rare earth ions in yttrium alumoborate. For example, YAB:  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$  can be used for solid-state lasers emitting in the visible range, YAB:  $\text{Nd}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$  can be used for lasers in the near infrared and YAB co-activated with  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  ions can be used for high-performance UV-visualizers [2] the demand for which in biological and medical research is growing.

We have fabricated and described in this paper a series of polycrystalline samples of YAB doped with  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Ce}^{3+}/\text{Tb}^{3+}$  ions. Colloid chemical approaches providing high homogeneity of the doped ions in host materials as compared to solid phase synthesis was used. Their phase composition, morphology and luminescence were investigated.

## 2. Experimental

Ultrafine yttrium alumoborate powders doped with cerium and terbium were prepared according to [3] by co-precipitation of metal hydroxides with ammonia from water solutions of appropriate salts of nitric acid with subsequent heat treatment in air. Solutions of nitrates of yttrium and aluminum were mixed in accordance with the stoichiometry of  $\text{Y}_2\text{O}_3:3\text{Al}_2\text{O}_3:4\text{B}_2\text{O}_3$ . The boric acid was added in 10 % excess to stoichiometry. Rare earth ions as activators were added as nitrate salts to a mixture of aluminum and yttrium nitrate solution at the amounts of 1 at.% Ce and 5 at.% or 10 at.% Tb of the substitutable  $\text{Y}^{3+}$  ions. The final co-precipitation of the hydroxides was allowed for a day. The precipitates formed were separated by centrifugation, washed with alcohol and dried in air at 60–80 °C. They were then heat treated in air at 600 °C for 2 h to remove structurally bound water and residual acid and at 1150 °C for 2 h to form yttrium alumoborate.

X-ray diffraction (XRD) analysis of the samples was performed with DRON-3 diffractometer using  $\text{CuK}\alpha$  radiation. The morphology and particle sizes were determined by scanning electron microscopy (SEM) in a LEO-1420 device. The luminescence spectra (LS) and luminescence excitation spectra (LES) were recorded at 298 K with a SDL-1 spectrofluorimeter.

## 3. Results and discussion

The crystal structure of the samples was found to correspond well to crystalline  $\text{YAl}_3(\text{BO}_3)_4$  with the huntite lattice. Owing to the small differences in ionic radii of  $\text{Y}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$ , the influence of the latter on the position of XRD reflections is small. According to SEM, the samples  $\text{YAl}_3(\text{BO}_3)_4$  doped with Ce and Tb are composed of 0.2–2  $\mu\text{m}$  particles. The average particle size of YAB sample containing 1 % Ce and 5 % Tb is about 0.5  $\mu\text{m}$  and of YAB sample containing 1 % Ce and 10 % Tb is about 1  $\mu\text{m}$ . The particles have a polygonal shape with a number of surfaces from 4 to 6 and the rod-like form. The size of the rod-shaped particles ranges from 0.2 to 1  $\mu\text{m}$ .

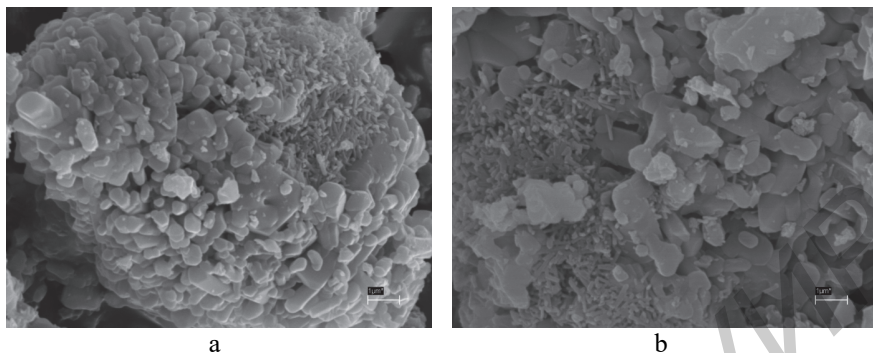


Figure 1. SEM of  $\text{YAl}_3(\text{BO}_3)_4$  samples containing: a – 1 % Ce + 5 % Tb, b – 1 % Ce + 10 % Tb.

The luminescence spectra of  $\text{Tb}^{3+}$  ions in mono-activated and co-activated with  $\text{Ce}^{3+}$  YAB samples at a concentration of  $\text{Tb} \geq 5$  at.% are only due to  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$  transitions (Fig. 2a). They practically do not depend on the concentration of doping elements. The absence of such relationship is due to sufficiently large minimum distance (Ln-Ln) and the recessed position of the  ${}^5\text{D}_4$  state.

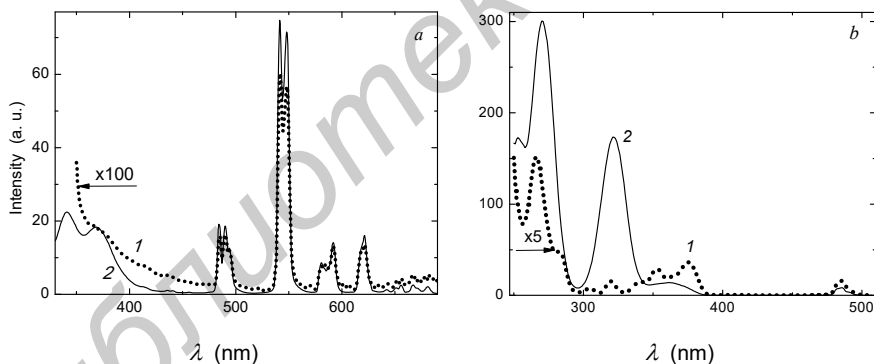


Figure 2. Corrected luminescence (a) and luminescence excitation (b) spectra of  $\text{YAl}_3(\text{BO}_3)_4$  polycrystals doped with (1)  $\text{Tb}^{3+}$  (5 at.%) and co-doped with (2)  $\text{Ce}^{3+}$  (1 at.%) and  $\text{Tb}^{3+}$  (5 at.%).  $\lambda_{\text{exc}} = 310$  nm (a),  $\lambda_{\text{rec}} = 545$  nm (b).

Low-intense luminescence excitation bands of ions in the region of 300–400 nm (Fig. 2b, curve 1) are due to  $f^8-f^8$  transitions. The two-humped band at 260 nm is due to  $4f^8 \rightarrow 4f^7({}^8S_{7/2})5d^1(E)$  transitions. At the excitation wavelength about 310 nm, the luminescence intensity of  $\text{Tb}^{3+}$  ions in the co-activated sample is of about two orders of magnitude higher than that in the mono-activated one (curves 1 and 2 in Fig. 2a). That indicates a sensitization of  $\text{Tb}^{3+}$  ions luminescence by  $\text{Ce}^{3+}$  ions. The efficiency of such sensitization

according to the ratio of the partial intensity of the  $Tb^{3+}$  luminescence in the integrated, including an additional band luminescence of  $Ce^{3+}$  (two-humped band at  $\lambda \leq 350$  nm), is about 50 %. Increasing of the concentration of  $Tb^{3+}$  ions up to 10 at.% with the constant concentration of  $Ce^{3+}$  ions (1 at.%) is followed by approximately 10 % increase in the efficiency of the sensitized luminescence of  $Tb^{3+}$  ions. The implementation of the described luminescence sensitization is confirmed by the luminescence excitation spectra (curves 1 and 2 in Fig. 2b) clearly demonstrating an emergence of two intense UV bands at 270 and 320 nm typical for  $Ce^{3+}$  ions in YAB.

#### 4. Conclusion

$YAl_3(BO_3)_4:Ce^{3+},Tb^{3+}$  polycrystals synthesized by colloid chemical approaches with average sizes of polygonal particles from 0.5 to 1.0  $\mu m$  are characterized by effective (50 % and higher) sensitizing of  $Tb^{3+}$  luminescence by  $Ce^{3+}$  ions. This allows application of such polycrystals for UV imaging.

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