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Influence of growth conditions on chemical composition and properties of borate crystals for laser application

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The influence of technological growth conditions on the formation of defects and color centers in $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals is investigated. According to the study of the optical properties and chemical analysis data the role of boron vacancy in the formation of color centers is determined.

Keywords: binary borate, color center.

Исследовано влияние технологических условий выращивания на образование дефектов и центров окраски в кристаллах $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd). Согласно данным исследования оптических свойств и данным химического анализа, определена роль вакансий бора в формировании центров окраски.

Вплив умов вирощування на склад і властивості лазерних кристалів боратів. *В.М.Баумер, Л.В.Гудзенко, М.Б.Космина, О.М.Шеховцов.*

Досліджено вплив технологічних умов вирощування на утворення дефектів і центрів забарвлення у кристалах $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd). Згідно з даними дослідження оптичних властивостей і даними хімічного аналізу, визначено роль вакансій бору у формуванні центрів забарвлення.

1. Introduction

The Czochralski method is one of technologies widely used in industrial production of large single crystals of good optical quality for many applications such as lasers, non-linear optics, scintillators and others [1]. The main criteria in choice of crystals for the successful growth by the Czochralski method are congruent melting of compounds and the absence of phase transformation. The principal problems to be solved at crystal growth are determination of typical defects for the crystal and correction of crystal growth technology to prevent defect formation. Defects as impurity phase inclusions, inhomogeneous composition, macro scale defects (crystal cracking, gas bubbles) will limit the use of a crystal ingot.

For the first time information about the growth of binary orthoborates $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals by the Czochralski method was reported in [2]. Later a number of papers there appeared where spectral-kinetic properties of $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals doped by Nd, Yb, Er were studied [3–6]. The lasing operation under flash lamp and laser (diode laser and Ti:sapphire laser) pumping were also demonstrated for different regimes [4, 7–10]. The lasers based on these crystals were shown to be promising for many scientific tasks and practical use.

But there remain certain problems to be solved for successful application of $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals. The authors of [11] have pointed out the typical defects of the crystals. A stria appeared in the central part of the crystals during the crystal growth and increased in size. The output of the stria free ingot was about 50 %. The excess boron additive did not affect the crystal quality. The authors assumed that this problem was connected to boron evaporation and the stoichiometric composition of the crystals does not melt congruently [11].

The authors of [11] have also reported poor quality of $Ca_3Y_2(BO_3)_4$ crystals because of precipitates distributed in the major part of the crystal bulk. Post growth annealing did not improve the optical quality and led to the crystal destruction. Moreover, the formation of $CaYBO_4$ phase was revealed at the surface of the Czochralski grown $Ca_3Y_2(BO_3)_4$ crystal. The authors supposed that it could be due to either thermal decomposition of the compound, or to the fact that congruent composition was not the stoichiometric one. But the data of differential thermal analysis did not confirm incongruent melting of the compound [12].

For these reasons this work is devoted to description of the crystal growth conditions, characterization of the chemical compositions, as well as of the study of colour centres in pure $Ca_3RE_2(BO_3)_4$ (RE = Y, Gd) crystals.

2. Experimental

To synthesize the $Ca_3RE_2(BO_3)_4$ charge the $CaCO_3$ (99.99 %), RE_2O_3 (99.99 %) (RE = Y, Gd) and B_2O_3 (99.95 %) compounds were used. The stoichiometric mixture of the initial reagents was placed into a platinum crucible and solid state synthesis was carried out according to the reaction:

$$3CaCO_3 + 2B_2O_3 + RE_2O_3 \rightarrow$$
$$\rightarrow Ca_3RE_2(BO_3)_4 + 3CO_2\uparrow (RE = Y, Gd).$$

The obtained material was finely ground. The produced $Ca_3RE_2(BO_3)_4$ charge was ground and placed in another crucible for crystal growth. Pure $Ca_3RE_2(BO_3)_4$ crystals were grown by the Czochralski method using an automated and equipped with a weight control system "Analog" puller. The growth processes was carried out in inert (argon) and oxygen containing (air) atmospheres. Ir and Pt crucibles were used for argon and air atmospheres, respectively. The pulling and rotation rates were 1–3 mm/h and 20–30 rpm, respectively. The crystals were grown along the crystallographic axis [001] (Fig. 1).

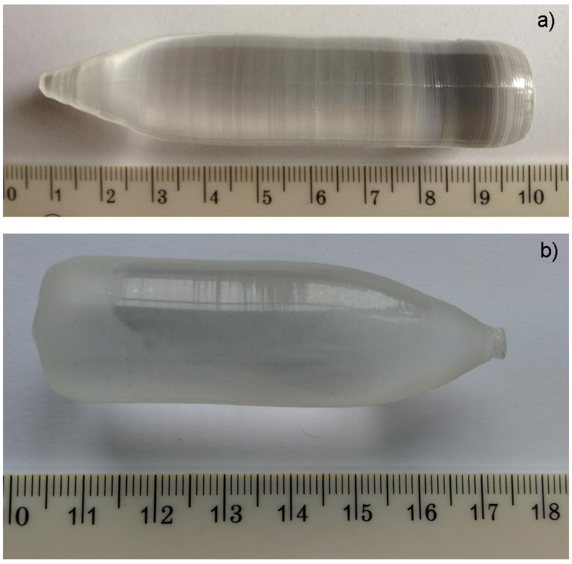

Fig. 1. $Ca_3RE_2(BO_3)_4$ (RE = Y, Gd) crystals: a — $Ca_3Y_2(BO_3)_4$ crystal grown in argon from Ir crucible; b — $Ca_3Gd_2(BO_3)_4$ crystal grown in air from Pt crucible.

The crystals investigated in the present study were grown under the same conditions, i.e. at fixed temperature gradient, rotation speed and pulling rate.

To determine the basic host elements of $Ca_3RE_2(BO_3)_4$ borates the special methods were developed. The single crystals were dissolved in a mixture of nitric and hydrochloric acids. For determination of the rare earth elements (Y or Gd) and the calcium concentrations, the complexometric method was used [13]. For $Ca_3Y_2(BO_3)_4$ crystal the yttrium concentration was determined by means of ethylenediamine acetic acid sodium salt (EDTA) titration in urotropin medium containing xylenol orange indicator at 5.6–5.6 pH. In the aliquot part of the solution the aggregated concentration of yttrium and calcium was determined using back titration of EDTA excess by zinc sulphate in ammonium chloride buffered medium at pH 10. The calcium content was calculated as the difference between the aggregated concentration and the Y concentration. For

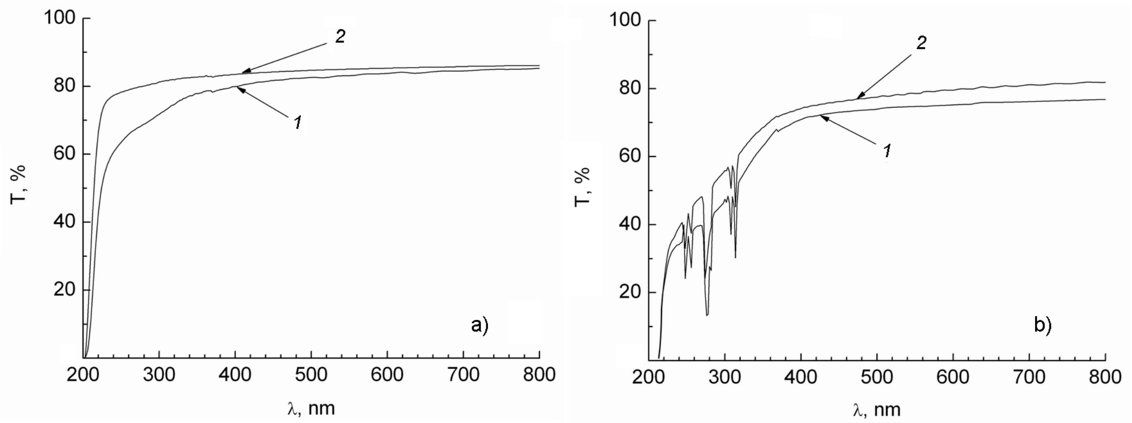

Fig. 2. Transmittance spectra of the $Ca_3RE_2(BO_3)_4$ (RE = Y, Gd) crystals grown in air (curve *1*) and argon (curve *2*): a — $Ca_3Y_2(BO_3)_4$, b — $Ca_3Gd_2(BO_3)_4$.

$Ca_3Gd_2(BO_3)_4$ crystals the calcium concentration was determined by means of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone extraction. Boron was determined by means of the alkalimetric method. Yttrium and gadolinium were masked by the addition of EDTA. EDTA concentration was equimolar to the stoichiometric concentration of yttrium or gadolinium. There was performed titration of boric glycerol acid with phenolphthalein indicator.

The Bragg-Brentano powder diffractometer (SIEMENS D-500) equipped with Cu tube was used for the investigation of X-ray diffraction in the crystals. The X-ray phase analysis was performed by Rietveld method using the program "Full Prof".

Optical absorption spectra were measured before and after irradiation using a "Perkin Elmer" spectrophotometer in the 200–1100 nm range. For irradiation X-ray source was used, the dose was 3000 R. The delay time after irradiation did not exceed 15 min. The induced absorption coefficient was calculated as $\Delta K = (D_{irr} - D)/h$, where D_{irr} and D are the optical densities after and before irradiation, respectively, h is the sample thickness.

3. Results and discussion

The transmission spectra of $Ca_3Y_2(BO_3)_4$ crystals grown in different atmospheres are presented in Fig. 2a. The fundamental band absorption edge for both $Ca_3Y_2(BO_3)_4$ crystals is the same (210 nm). The $Ca_3Y_2(BO_3)_4$ crystal grown in oxygen-containing atmosphere demonstrates the additive absorption in the range of 240–340 nm.

The same situation has been observed for $Ca_3Gd_2(BO_3)_4$ crystals (Fig. 2b). The fundamental band absorption edge for both $Ca_3Gd_2(BO_3)_4$ crystals is the same (220 nm), but the transmittance for $Ca_3Gd_2(BO_3)_4$ crystal grown in air is worse. The additive absorption in the range of 240–380 nm region is observed for both crystals, but for $Ca_3Gd_2(BO_3)_4$ crystal grown in air the additive absorption is more intensive.

Since the colour centres are formed more effectively in the crystals where the composition deviates from the stoichiometric one, the chemical analysis of the grown crystals has been done.

For both $Ca_3Y_2(BO_3)_4$ crystals grown in inert and air atmospheres the boron deficit was established (Table 1). Pronounced boron deficit was detected for $Ca_3Y_2(BO_3)_4$ crystal

Table 1. Concentrations of host elements for $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals

Crystal		Host element concentrations, wt %		
		RE	Ca	B
$Ca_3Y_2(BO_3)_4$	Stoichiometry	33.3	22.5	8.1
	Argon	33.3±0.1	22.3±0.1	7.9±0.1
	Air	33.4±0.1	22.2±0.1	7.6±0.1
$Ca_3Gd_2(BO_3)_4$	Stoichiometry	46.9	17.9	6.5
	Argon	45.3±0.1	18.5±0.1	6.2±0.1

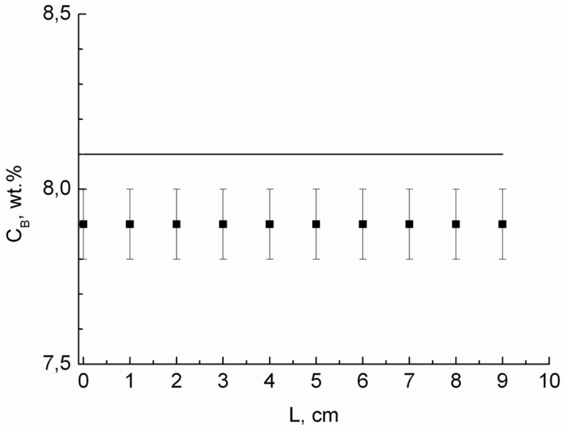

Fig. 3. Distribution of boron along the $Ca_3Y_2(BO_3)_4$ crystal. The solid line corresponds to the stoichiometric boron concentration.

grown in air. The small calcium deficit was observed for both $Ca_3Y_2(BO_3)_4$ crystals, too. For $Ca_3Y_2(BO_3)_4$ crystal the Ca/Gd balance deviates from the stoichiometric composition toward calcium excess and gadolinium deficit. The boron concentration for $Ca_3Y_2(BO_3)_4$ crystal is lower than the stoichiometric one (Table 1).

It may be concluded that the additive absorption in the range of 240–380 nm is caused by the color centers based on boron vacancies. Moreover, higher concentrations of the boron vacancies are observed in the crystals grown in air. This effect may be due more intensive boron evaporation in the acid containing medium (air atmosphere) [14].

According to the hypothesis of the authors, one of the causes for the formation of striae and opaque areas in the crystals was the deviation from the stoichiometric composition due to evaporation of boron. The analysis of the host element concentration for the $Ca_3Y_2(BO_3)_4$ crystal with the length of 90 mm showed the following results. In the upper part of the crystal the deviation from the stoichiometric ratio of Ca/Y was no more 5 %, in the bottom part of the crystal – 9 %. At the same time, the boron concentration was constant along the crystal (Fig. 3).

Thus, the cause of a poor optical quality of $Ca_3RE_2(BO_3)_4$ (RE = Y, Gd) crystals may be connected with the use of the charge where the formation of the $Ca_3RE_2(BO_3)_4$ (RE = Y, Gd) phases is not completed. We have observed the defects reported by the authors [11] when the charge synthesized according to the conditions described in [11, 12] was used.

For example, the use of such $Ca_3Y_2(BO_3)_4$ charge led to crystallization of intermediate phases with a higher melting temperature. The formation of striae and opaque part in the bulk of the crystal was observed for $Ca_3Y_2(BO_3)_4$ crystal due to crystallization of YBO_3 and $CaYBO_4$ phases in the core of cylindrical part [15]. The $REBO_3$ (RE–La, Sm, Eu, Yb, Lu) orthoborates were detected as intermediate phases at solid state synthesis of $Ca_3RE_2(BO_3)_4$ (RE–La, Sm, Eu, Yb, Lu) borates. Moreover, after post growth annealing in air the hexagonal $REBO_3$ (RE = Y, Gd) and amorphous $Ca(BO_2)_2$ phases were detected on the crystal surface for $Ca_3RE_2(BO_3)_4$ (RE = Y, Gd) crystals with maximum boron deficit.

The problem of the charge synthesis was solved by means of long-term thermal treatment of the reagent mixture at different temperatures taken from [16]. Using the charge containing 95–97 wt % of the $Ca_3Y_2(BO_3)_4$ phase, the single crystals with the volume 60–70 % of the melt volume were grown (Fig. 1). According to the X-ray diffraction data, $Ca_3RE_2(BO_3)_4$ (RE = Y, Gd) crystals were free of impurity phases. The losses of the melt during the growth of $Ca_3RE_2(BO_3)_4$ (RE = Y, Gd) crystal were less than 1 wt %.

The induced colour centre formation affects negatively the functional characteristics of active lasing elements, reduces the lifetime of devices. The efficiency of the induced colour centre formation in crystals depends on many factors such as the chosen growth technique and growth conditions, impurities, peculiarities of the crystal structure, etc, for example [17].

Pure $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals are getting colouring effectively after X-ray irradiation. The induced absorption coefficients ΔK for the $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals are presented in Fig. 4. For both crystals the induced absorption peak is the superposition of elementary peaks and the maximums of induced absorption being located at 440 and 400 nm, respectively. The Gauss decomposition was done and the best fitting was obtained at the decomposition into three Gaussians for both crystals. Each Gaussian can be assigned to one kind of induced colour centre. But Gaussian could also originate from two or more centres.

Bleaching of the crystals started at 120°C and after annealing at 180°C the optical transmission regained to the initial values. The TSL signal was not observed for both undoped $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd)

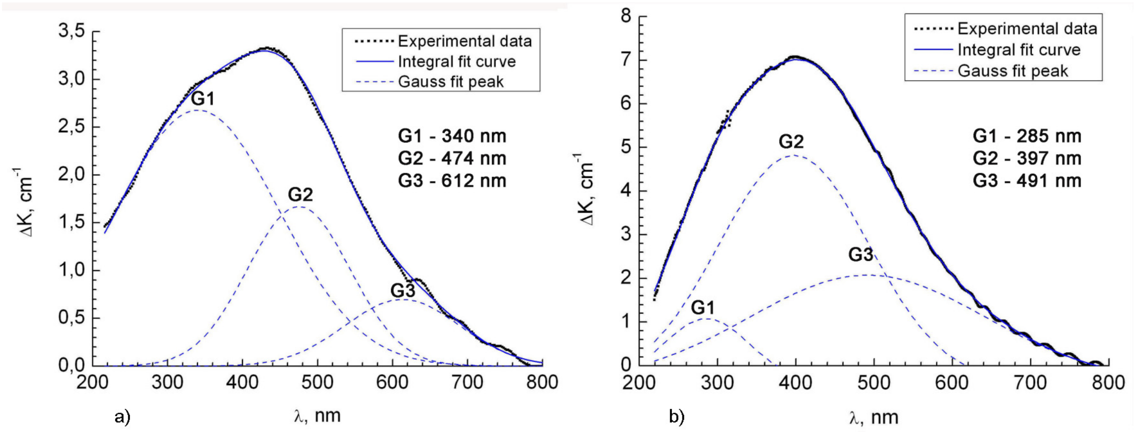

Fig. 4. The induced absorption coefficients ΔK for the crystals grown in argon: a — $Ca_3Y_2(BO_3)_4$, b — $Ca_3Gd_2(BO_3)_4$.

Table 2. Concentration of boron vacancies in $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals grown in argon

Crystal	$Ca_3Y_2(BO_3)_4$	$Ca_3Gd_2(BO_3)_4$
Concentration of boron vacancies V_B, cm^{-3}	$4.17 \cdot 10^{20}$	$7.4 \cdot 10^{20}$

crystals in 200–750 nm spectral and 50–400°C temperature ranges.

It should be noted that the induced absorption coefficient ΔK for the $Ca_3Gd_2(BO_3)_4$ crystal (Fig. 4b) is approximately twice as high as the one for $Ca_3Y_2(BO_3)_4$ crystal (Fig. 4a) at the same dose. This correlates well with the higher concentration of boron vacancies in $Ca_3Gd_2(BO_3)_4$ crystal in comparison with $Ca_3Y_2(BO_3)_4$ crystal (Table 2). Thought the positions of maxima of induced absorption for both crystals are close, the positions of Gaussian bands are different (Fig. 4). Therefore we can consider that the origin of induced colour centres in $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals is the same and is involved with the boron vacancies.

4. Conclusions

The formation of defects (striae and impurity phases) in the $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals is caused by the use of the charge where the synthesis of $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) compounds is not complete. It is established that the chemical composition of $Ca_3RE_2(BO_3)_4$ crystals deviates from the stoichiometric one. For $Ca_3Y_2(BO_3)_4$ crystal a small deficit of calcium and boron is observed. For $Ca_3Gd_2(BO_3)_4$ crystal the Ca/Gd balance deviates from the stoichiometric composition toward calcium excess and gadolinium deficit. The boron deficit is higher than the one for $Ca_3Y_2(BO_3)_4$ crystal. $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals grown in air are characterized by the higher boron deficit and worse optical transmittance in comparison with those for the crystals grown in argon. The assumption has been done that the origin of induced colour centres in $Ca_3RE_2(BO_3)_4$ (RE–Y, Gd) crystals is involved with the boron vacancies.

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