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TITLE: International Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals Held in Zakopane, Poland on 9-12 October 2000

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Optical properties of some borate single crystals

A. Majchrowski[a*], T. Łukasiewicz[b], Z. Mierczyk[c], M. Malinowski[d]

a - Institute of Applied Physics MUT, ul. Kaliskiego 2, 00-908 Warsaw, Poland
b - Institute of Electronic Materials Technology, ul Wólczyńska 133, 01-919 Warsaw, Poland
c - Institute of Optoelectronics MUT, ul. Kaliskiego 2, 00-908 Warsaw, Poland
d - Institute of Microelectronics and Optoelectronics PW, ul. Koszykowa 75, 00-662 Warsaw, Poland

ABSTRACT

This paper describes efforts taken in Institute of Applied Physics and Institute of Electronic Materials Technology to obtain several single crystals from borate family, namely $CsLiB_6O_{10}$ (CLBO), $Ca_4GdO(BO_3)_3$ (GdCOB), $Li_2B_4O_7$ (TBO), β-BaB_2O_4 (BBO), and $YAl_3(BO_3)_4$ (YAB), pure and doped with several ions. The main goal of this investigation was to develop technology of these new nonlinear optical materials to create possibility of their applications in higher harmonics generators and self-frequency doubling lasers. Depending on such properties of crystallized borate materials as incongruent melting or high temperature phase transitions, Czochralski technique or high temperature solution growth technique were used. The main aspects of crystallization of these materials as well as their optical properties are discussed.

keywords: borate single crystals, high temperature solution growth, Czochralski growth, nonlinear optical materials.

1. INTRODUCTION

Recent tremendous advances in the area of solid state lasers and nonlinear optics have been mainly driven by the development of new materials, having better properties than standard materials. Very important group of these new materials are borate single crystals, which possess excellent properties such as high damage threshold for laser radiation, high coefficients of second and higher harmonics generation, transparency far into ultraviolet, high optical quality, and good chemical and mechanical stability.

Borate crystals exist in many structural types due to three-fold (trigonal) or four-fold (tetrahedral) coordination of boron atoms in boron-oxide compounds.[1] Various anionic groups as basic structural units cause the existance of different structures of borates, what gives the possibility of selecting appropriate materials for chosen applications. Borates find many applications as substrates for Surface Acoustic Wave (SAW) devices, and dosimetric, nonlinear and lasing materials. The most interesting feature of borates are their nonlinear optical (NLO) properties. Powerful, tunable ultraviolet sources required for many applications (spectroscopy, data storage, remote sensing, medicine etc.) rely on frequency-doubling of lasers working in the visible range.

The wavelength range of solid state lasers has been greatly increased due to parametric conversion, nonlinear mixing, and higher harmonics generation. All these applications depend on the development of new NLO materials. As it was mentioned earlier borates have properties which fulfil conditions required for good NLO materials. According to Chen[1] the following anionic groups as basic structural units in borate crystals are of practical interest $(BO_3)^{3-}$, $(BO_4)^{5-}$, $(B_2O_5)^{4-}$, $(B_2O_7)^{8-}$, $(B_3O_6)^{3-}$, $(B_3O_7)^{5-}$, $(B_3O_8)^{7-}$, $(B_3O_9)^{9-}$, $(B_4O_9)^{6-}$ and $(B_5O_{10})^{5-}$. Chen's calculations have shown that planar anionic groups containing conjugated π-orbital systems (e.g. $(B_3O_6)^{3-}$) are more favorable to the appearance of large second-order susceptibilities (influencing SHG coefficients), compared with the non-planar tetrahedral groups. On the other hand absorption edges of the planar groups lie within the wavelength range of 190-200 nm, while those of non-planar groups move towards shorter wavelengths up to 160 nm. The discovery of β-BaB_2O_4 (BBO)[2] triggered intensive researches in the area of nonlinear borates. As a result a group of promising NLO materials has been found, among which the most interesting are: LiB_3O_5 (LBO),[3] CsB_3O_5 (CBO),[4] $CsLiB_6O_{10}$ (CLBO),[5] $KBe_2BO_3F_2$ (KBBF),[6] and $Sr_2Be_2B_2O_7$ (SBBO).[7] They find applications in second harmonic generation, sum or difference frequency mixing and optical parametric oscillators. Borates are also very attractive as host materials for many dopants, due to possibility of substitution of some ions in host lattices by, for example neodymium or chromium ions. The substitution forms lasing materials with nonlinear behavior, what gives as a result self-frequency doubling materials.

* e-mail: amajchrowski@altair.geo.wat.waw.pl

Intl. Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals, Antoni Rogaski, Krzysztof Adamiec, Pawel Madejczyk, Editors, Proceedings of SPIE Vol. 4412 (2001) © 2001 SPIE · 0277-786X/01/$15.00

The most promising of these materials are: $Nd_xY_{1-x}Al_3(BO_3)_4$ (NYAB),[8] $YAl_3(BO_3)_4$:Cr (YAB:Cr),[9] $GdAl_3(BO_3)_4$:Cr (GAB:Cr)[10] with huntite structure and $Ca_4GdO(BO_3)_3$:Nd (GdCBO:Nd)[11] and $Ca_4Y(BO_3)_3$:Nd (YCBO)[12] from oxoborates family. Y and Gd do not show absorption in the wavelength range interesting for NLO applications and can be easily substituted by lasing ions, in some cases up to 15%, without modification of the accentric host lattice. They are presently intensively investigated as candidates for self-frequency doubling laser crystals. The progress in borate crystals investigations is so great, that every month new borate crystals are reported. In a very detailed review, dealing with borate crystals, Becker[13] gives information concerning more than 20 borate single crystals – and since that time new efficient NLO borates have been reported. This paper describes efforts of our group in the area of borate crystal growth and characterisation.

2. BORATE SINGLE CRYSTALS GROWTH

In Tables 1, and 2 some properties of chosen NLO and self-frequency doubling borates are given, respectively. $K_2Al_2B_2O_7$[14] and BiB_3O_6[15] are new NLO borates having good properties. BiB_3O_6 is specially promising material due to its very high SHG coefficient, although in our opinion it may suffer from rather small damage threshold.

Investigations of borates crystallisation have been carried out in our group for last decade. The first borate material obtained by us was $Li_2B_4O_7$[16], at that time it was sought for its applications in SAW devices. Recently $Li_2B_4O_7$ has been found to have good NLO properties, namely very high damage threshold for laser radiation and generation of UV radiation due to fourth and fifth harmonics. Good quality $Li_2B_4O_7$ single crystals, free from twinning, were obtained by the Czochralski method.

Single crystals of β-BaB_2O_4, which up till now is one of the most frequently used NLO materials, were also obtained by our group. The material undergoes phase transition at 925°C, and we used both top seeded solution growth (TSSG)[17] and Czochralski growth from supercooled stoichiometric melts[18] to obtain low-temperature phase of BBO.

For last two years we have been investigated three relatively new borate single crystals, $CsLiB_6O_{10}$, $Nd_xY_{1-x}Al_3(BO_3)_4$, and $Ca_4GdO(BO_3)_3$:Nd. Both TSSG and Czochralski technique were used, depending on properties of grown crystal. TSSG experiments were carried out in multi-zone resistance furnaces having high heat capacity. Precise temperature regulation, down to 0.01 K/hr linearly, was possible due to Eurotherm 906S regulators/programmers. Czochralski growth, depending on the melting point of the investigated material, was carried out using resistance or r.f. heating.

2.1. $CsLiB_6O_{10}$

CLBO is a congruently melting material (1118 K) with very high damage threshold for laser radiation. Both, TSSG technique using 5 mol.% of Cs_2O:Li_2O (1:1 molar ratio) self-flux diminishing very high viscosity of the molten material, and Czochralski technique, were used in our experiments. The temperature during CLBO crystallisation was lowered linearly at the rates 0.01-0.1 K/hr. When TSSG was used crystals grew into the melt, in case of Czochralski method crystals were pulled up 2mm/day. The rotation rate did not exceed 5 rpm. Czochralski grown CLBO crystals were 20-30 mm in diameter and 50 mm long.

The transparency of investigated CLBO crystals was far into UV. We found that at 190 nm the transmission of 3.3 mm thick CLBO sample was 86%, what is in good agreement with literature – see Tab. 1. CLBO is slightly hygroscopic, but careful storage stops the harmful influence of moisture. Second harmonic generation for 1.06 μm YAG:Nd laser radiation was obtained in our CLBO crystals.

2.2. $Nd_xY_{1-x}Al_3(BO_3)_4$

NYAB crystals combine both NLO and lasing properties. 1.06 μm laser oscillations in NYAB are then self-frequency doubled to 0.53 μm in the same crystal. NYAB melts incongruently, what imposes the necessity of TSSG from high temperature solutions. As flux $K_2Mo_3O_{10}$ was used. The starting composition was 20 mol.% of NYAB in $K_2Mo_3O_{10}$ with 5 at.% of neodymium in NYAB. The growth was carried out in multi-zone resistance furnaces in very low temperature gradients. The temperature was lowered at the rate 2.4 K/day in the range of 1323 – 1223 K. Growing crystals were rotated at the rate of 100 rpm. Typical growth lasted 3-4 weeks. As-grown crystals 1.5x1.5x1.0 cm have inclusions in the central parts but the outer parts of the crystals were transparent.

2.3. $Ca_4GdO(BO_3)_3$:Nd

GdCBO also posseses self-frequency doubling properties. The main advantage of GdCBO, comparing with NYAB, is relatively easy growth from stoichiometric melts – the material melts congruently at 1753 K. GdCBO single crystals, pure and doped with neodymium up to 7 at.%, have been grown by the Czochralski technique with use of MSR-2 puller equipped in r.f. generator. Crystals were grown on [010] seeds in pure nitrogen atmosphere. Single crystals up to 20 mm in diameter and 60 mm long, free of macroscopic defects were obtained.

3. SPECTROSCOPIC INVESTIGATIONS

Plane-parallel plates 1 mm thick were cut from obtained borate single crystals. In order to determine absorption coefficient dependence on wavelength k(λ) of the examined samples, the transmission measurements as a function of wavelength were performed. The measurements were carried out using the LAMBDA2 PERKIN ELMER spectrophotometer within the spectral range of 200÷1100 nm (Δλ=1 nm), the ACTA MVII BECKMAN spectrophotometer within the range of 1100÷1500 nm (Δλ=1 nm), and the Fourier PERKIN ELMER spectrophotometer 1725-X FT-IR within the range of 1.5÷25 μm ($\Delta 1/\lambda = 1\ cm^{-1}$) On the basis of the transmission T(λ) measurements of the samples, an absorption coefficient was calculated with consideration of multiple reflections of radiation inside a sample. The absorption spectra of investigated crystals are shown in Fig. 1 and Fig. 2.

a)

b)

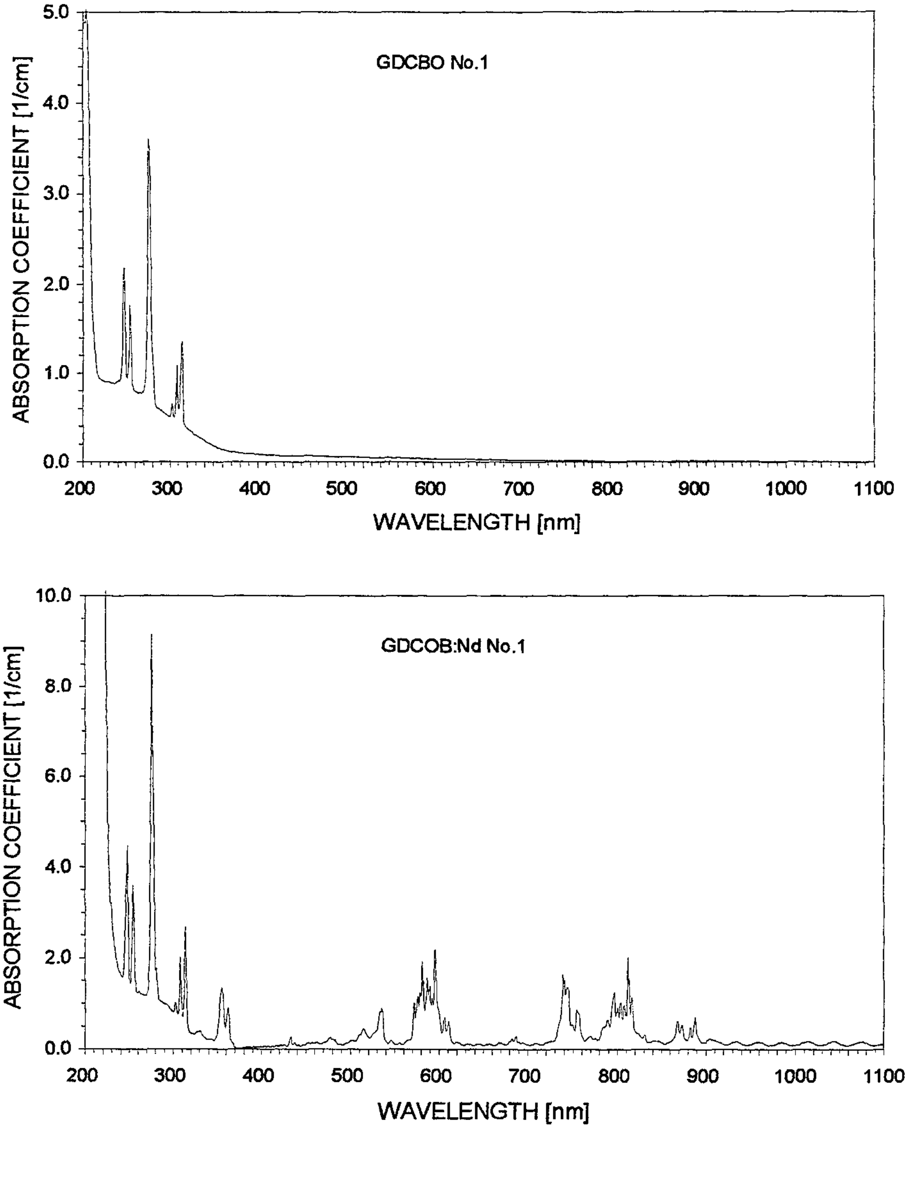


Fig. 1. Absorption spectra of undoped (a) and 3 at. % Nd^{3+} doped (b) GdCOB crystals

Tab. 1. Borates for SHG.[13,14,15]

MATERIAL	SPACE GROUP	TRANSPARENCY nm	SHG COEFF. pm/V	DAMAGE THRESHOLD GW/cm^2	METHOD OF CRYSTALLISATION
β-BaB_2O_4 (BBO)	R3c	190-2500	2.3	5 (10ns)	FLUX CZOCHRALSKI
LiB_3O_5 (LBO)	$Pna2_1$	155-2600	0.85	>0.9 (9ns)	SELF-FLUX
$CsLiB_6O_{10}$ (CLBO)	I42d	180-2750	0.95	26 (1ns)	SELF-FLUX CZOCHRALSKI
$Li_2B_4O_7$ (LTB)	$I4_1cd$	200-3500	0.55	40 (10ns)	CZOCHRALSKI BRIDGMAN
$Sr_2Be_2B_2O_7$ (SBBO)	P6c2	160-3780	1.7	-	SELF-FLUX
$K_2Al_2B_2O_7$ (KAB)	P321	180-	<SBBO	-	SELF-FLUX
BiB_3O_6 (BiBO)	C2	250-2300	3.2	-	CZOCHRALSKI

Tab. 2. Self-frequency doubling borates.[13]

MATERIAL	SPACE GROUP	TRANSPARENCY nm	SHG COEFF. pm/V	METHOD OF CRYSTALLISATION
$Nd_xY_{1-x}Al_3(BO_3)_4$ (NYAB)	R32	200-5000	1.28	FLUX
$Ca_4GdO(BO_3)_3$:Nd (GdCBO:Nd)	Cm	320-2700	0.56	CZOCHRALSKI
$Ca_4YO(BO_3)_3$:Nd (YCBO:Nd)	Cm	220-	1.1	CZOCHRALSKI

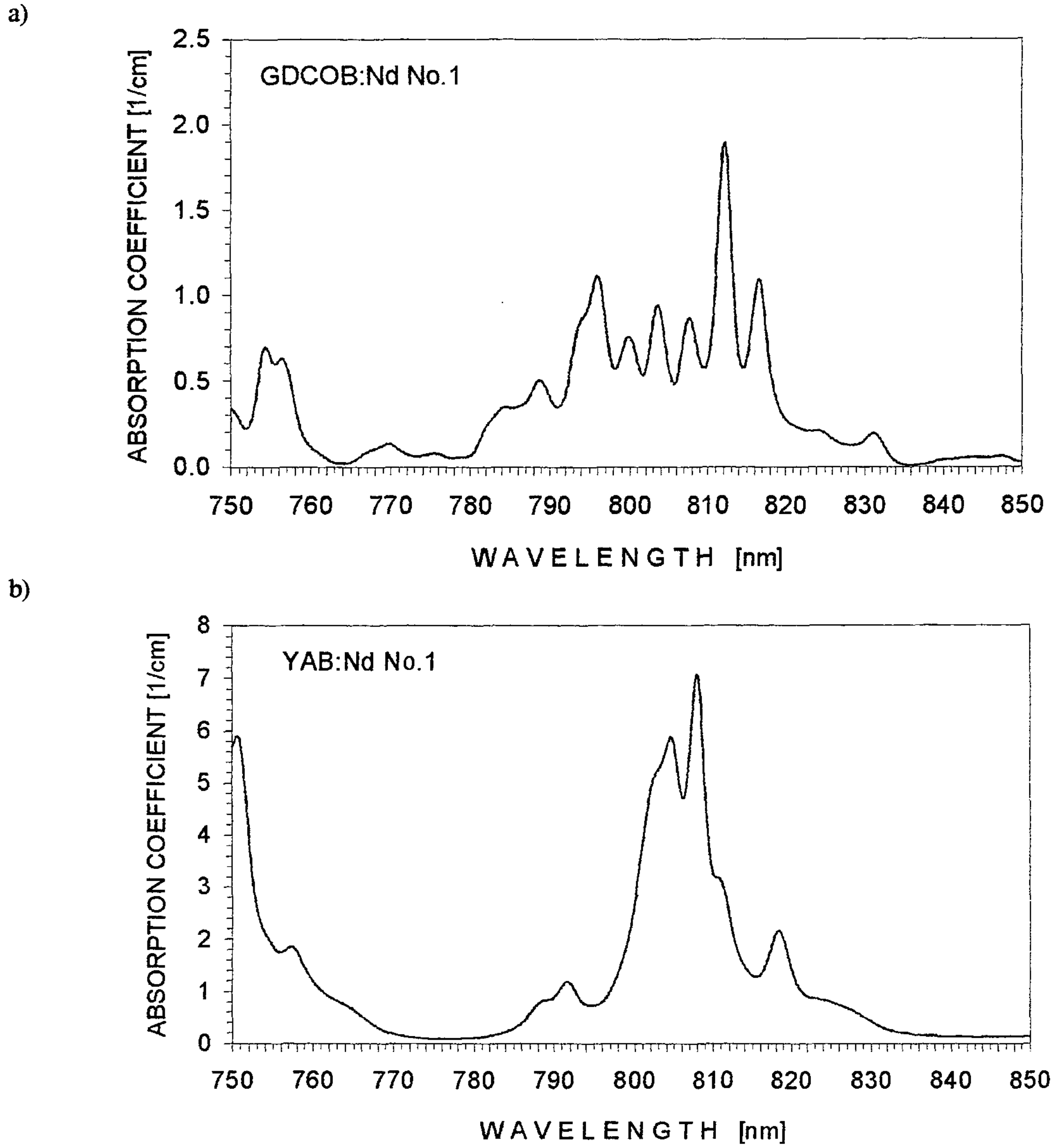


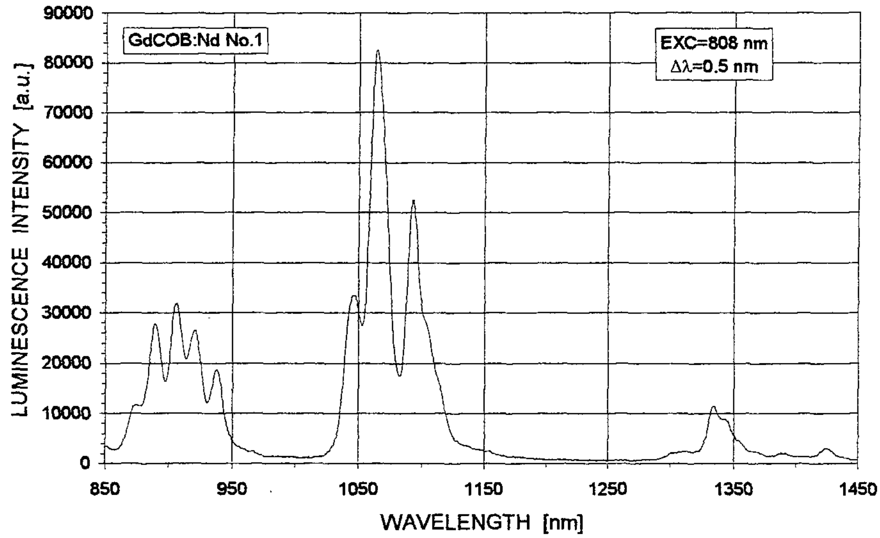
Fig. 2. Absorption spectra of neodymium doped borate crystals in 750÷850 nm region ($\Delta\lambda$=0.1 nm)
a) GdCOB:Nd^{3+} (3 at.% Nd^{3+}), b) YAB:Nd^{3+} (5 at.% Nd^{3+}).

The measurements of luminescence spectra have been performed in the system with the H20 JOBIN YVON monochromator (focal length 200 mm). In the excitation channel the laser diode emitting at 808 nm was applied. Luminescence excited with laser radiation, after spectral splitting in H20 monochromator with holographic gratings, was registered by means of the LOCK-IN (STANFORD RESEARCH SR510) system with thermoelectrically cooled InGaAs detector. Luminescence spectra of neodymium doped borate crystals are presented in Fig. 3. The measurements of of Nd^{3+} ions lifetime at the upper laser level ($^4F_{3/2}$) for the samples of neodymium doped borate crystals were made by means of direct method with pulse excitation.

The investigated medium was excited with radiation pulse duration significantly shorter than the lifetime τ at the excited level. After excitation a population level decay occurs, the evidence of which is fluorescence decay that can be observed. As a source of 808 nm diagnostic pulses SDL2430 laser diode was used. The laser was supplied from the power supply SDL800, controlled by a pulses generator. Generated pulses of 8 μs duration and 0.66 kHz frequency.

In the detection channel, perpendicular to the excitation channel, the silicon photodiode was applied and time characteristics of fluorescence decay were registered with the digital oscilloscope LeCROY 9350AM (500 MHz). The time-constant τ (fluorescence decay time) corresponds to the time after which the fluorescence intensity I reaches the I_0/e value. The results of measurements of fluorescence decay time in the investigated samples are listed in Table 3.

a)



b)

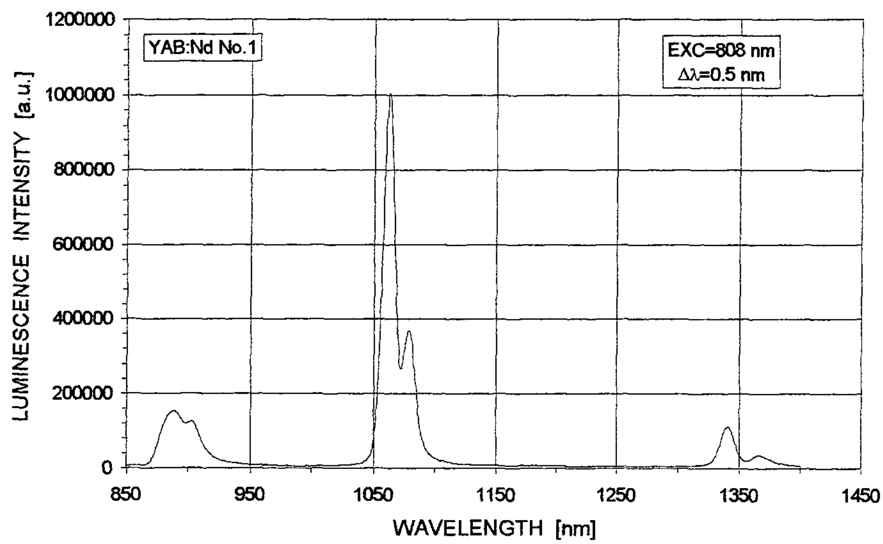


Fig. 3. Luminescence spectra of neodymium doped borate crystals a) GdCOB:Nd^{3+} (3 at.% Nd^{3+}), b) YAB:Nd^{3+} (5 at.% Nd^{3+}).

Tab. 3. Results of measurements of fluorescence decay time (level $^4F_{3/2}$) in the investigated crystals.

Crystal	Fluorescence decay time
GdCOB:Nd (3 at.% Nd^{3+})	78 ± 2 μs
YAB:Nd (5 at.% Nd^{3+})	57 ± 2 μs

4. CONCLUSIONS

Nonlinear optical and lasing borates crystallisation, namely CLBO, NYAB, and GdCBO:Nd, was investigated. Top seeded solution growth and Czochralski method were used to grow borate crystals. Optical and spectroscopic properties of as-grown crystals show their applicability both in second harmonic generation (SHG), and in self-doubling frequency of laser radiation.

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