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Spectroscopic studies of $Ln_2Ca_3B_4O_{12}$-Nd^{3+} (Ln=Y, La, Gd) crystals

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Abstract

In this work, the neodymium doped double borate single crystals $Ln_2Ca_3B_4O_{12}$-Nd (Ln=La, Gd, Y) were Czochralsky grown. Their structure, spectroscopic characteristics, and lifetimes were studied. The distribution coefficients of neodymium ions into the borate lattice $Ln_2Ca_3B_4O_{12}$-Nd (Ln=La, Gd, Y) were determined. They are close to 1 and slightly increase in the series La, Gd, Y in accordance with the change in the melting temperature. Using the Judd–Ofelt method we determined the intensity parameters: $\Omega_2=4.56\times10^{-20}$ cm^2 and 4.59×10^{-20} cm^2; $\Omega_4=7.29\times10^{-20}$ cm^2 and 7.56×10^{-20} cm^2, and $\Omega_6=9.87\times10^{-20}$ cm^2 and 10.76×10^{-20} cm^2 for $La_2Ca_3B_4O_{12}$-Nd and $Gd_2Ca_3B_4O_{12}$-Nd, respectively,. The microparameters and selfquenching rate in the $La_2Ca_3B_4O_{12}$-Nd and $Gd_2Ca_3B_4O_{12}$-Nd crystals were calculated. It was shown that the neodymium selfquenching could be described within the framework of the static model, which, probably, corresponds to the structural properties. The possible application of the studied crystals as active laser media, including also the laser-diode pumped ones was concluded. © 1998 Elsevier Science B.V.

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1. Introduction

The lanthanide, aluminium, or scandium double borate crystals $Ln_2A_3B_4O_{12}$-Nd (Ln=La–Lu, Y, A=Al and Sc) are known as the active laser media for the lamp and laser-diode pumped lasers [1,2]. In this work the spectroscopic properties of the rare-earth and calcium double borates $Ln_2Ca_3B_4O_{12}$-Nd (Ln=La, Gd, Y) were studied. Single crystals were Czochralsky grown from a melt, their crystallographic structure, absorption and luminescence spectra, and lifetimes were investigated, intensity parameters were obtained by the Judd–Ofelt technique.

The possibility to obtain the crystals highly-doped with neodymium without lowering their optical quality, which reveal wide structureless absorption bands in the laser-diode emission band peaked at 805 nm, permits to make the conclusion on their possible use as the laser-diode pumped active laser media tuneable within the luminescence linewidth.

2. Structure and synthesis

The highly pure Ln_2O3, $CaCO_3$, and H_3BO_3 were used as parent crystals. Thoroughly mixed pressed mixtures with a stoichiometric composition were slowly heated (100° h^{-1}.) to 500°C and further to the synthesis temperature at the rate 300° h^{-1}. Duration of the synthesis was 5–8 h; cooling down to 900°C was performed at the rate 200–300° h^{-1} and then in the switched off furnace.

The mixture was synthesized in the Pt crucible at 1000°C during 5 h (slow heating to 500°C in order to avoid the B_2I_3 losses upon too fast H_3BO_3 decomposition). The $Ln_2Ca_3B_4O_{12}$ single crystals were Czochralsky obtained with a 'Malvern MSR-2' (Metals Research) automatic set-up in the Pt-crucibles with the 35 mm diameter and 35 mm length including the 60–80 g of the melt.

Seeding was performed on the Pt-wire. Pulling rate made 4–5 mm h^{-1} for pure and 2–3 mm h^{-1} for the Nd^{3+} doped crystals, rotation rate was 20–40 rpm.

Melting temperatures (t_m) of $Ln_2Ca_3B_4O_{12}$ lower with a decrease in the Ln^{3+} ion radius from 1425°C (Ln) [3] to <1200°C(Lu). The melting is congruent, the crystallized melt consist of $Ln_2Ca_3B_4O_{12}$. The congruent composition does not coincide with the stoichiometric one, which is confirmed by the lowering crystal quality in the end of crystallization. Deviation from the stoichiometry for the $La_2Ca_3B_4O_{12}$ and $Gd_2Ca_3B_4O_{12}$ is low, being somewhat higher for $Y_2Ca_3B_4O_{12}$. In accordance with the changes in the t_m in the $Ln_2A_3B_4O_{12}$ series, one can expect $K_{Nd}<1$ in $La_2A_3B_4O_{12}$ and $K_{Nd}>1$ in $Gd_2Ca_3B_4O_{12}$ and

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$Y_2Ca_3B_4O_{12}$, which was confirmed by the electron-probe analysis.

Pure and Nd doped $Ln_2Ca_3B_4O_{12}$-Nd (Ln=La, Gd, Y) single crystals with a 13–18 mm diameter and up to 100 mm length were grown. Crystals have no cleavages and show intermediate position in hardness between the quartz and lithium niobate. They are inert to water, however, soluble in the diluted mineral acids.

The rare-earth and alkali-halide double borates $Ln_2A_3B_4O_{12}$ (Ln=La-Lu and Y; A=Ca, Sr, Ba) [4–6] crystallize in the rhombic system and are, probably, isostructural excepting the $Yb_2A_3B_4O_{12}$ ones [7].

Experimental crystallographic properties of the $La_2Ca_3B_4O_{12}$ crystals are as follows: space group-Pnma; unit cell parameters-a=7.242, b=16.129, and c=8.688 Å; volume V=1014.8 nm^{-3}; and density d=4.145 g cm^{-3}. In determining the $La_2Ca_3B_4O_{12}$ structure we used the model reported in [8] for $La_2Ca_3B_4O_{12}$ which allowed for similarity of the lattice metrics, symmetry, and results of testing the $Ln_2Ca_3B_4O_{12}$ crystals for piezoelectric effect and laser second harmonic generation.

3. Optical properties

3.1. Nd distribution coefficient in $La_2Ca_3B_4O_{12}$-Nd (Ln= La, Gd, Y) crystals

Since the distribution coefficient of neodymium into the borate crystals was unknown, we have developed a simple non-destructive spectro-photometric method of obtaining the neodymium average concentration. We also determine the effective distribution coefficient K_{Nd} from the measured peak optical density D_λ at a probe band with a wavelength λ and the known peak absorption cross section $\sigma_a(\lambda)$ by the method reported in [9]. Average neodymium concentration N_{Nd} in a sample with the length L was calculated by formula: $N_{nd}[cm^{-3}]=2.3\ D_\lambda(L[cm].\sigma_a(\lambda)[cm^2])^{-1}$.

The absorption technique was calibrated on the model crystal samples formed as thin polished plates with the known concentration for which the absorption spectra were recorded with a Perkin–Elmer Lambda-9 spectrophotometer and the peak absorption cross sections $\sigma_a(\lambda)$ were determined. The neodymium concentration in the model samples was determined by the X-ray spectral analysis with the electron-probe microanalyzer Camebax by CAMEKA. The fragments of the absorption cross section spectra with the probe band are shown in Fig. 1a and Fig. 1b. As results from the experiments, the effective neodymium distribution coefficient K_{Nd} into the $La_2Ca_3B_4O_{12}$-Nd (Ln=La, Gd, Y) lattice are close to 1, somewhat increasing in the series La, Gd, Y that corresponds to the changes of tm in the series. They are 0.94, 1.12, and 1.2, respectively. Increase of K_{Nd} in the series corresponds to the decreasing of the ionic radii of La, Gd, and Y. According to the electron-probe analysis of the Nd^{3+} doped $La_2Ca_3B_4O_{12}$ and $Gd_2Ca_3B_4O_{12}$ crystals, the ratio Nd/(Nd+La) equals, respectively, 4.7 and 5.6 at% (being 5% in the melt) which agrees with the above results.

3.2. Optical transition intensities

The $La_2Ca_3B_4O_{12}$ and $Y_2Ca_3B_4O_{12}$ are nearly transparent in the 210–2500 nm range, weak vibrational bands of host absorption being observed in 2500–3125 nm. Along with this, the spectrum of $Gd_2Ca_3B_4O_{12}$ shows the UV bands of intrinsic host absorption corresponding to the $^8S_{7/2}\rightarrow{}^6D_j$, ^6I_j, ^6P_j transitions in Gd^{3+}.

We have studied the absorption and luminescence spectra and the lifetimes in the $La_2Ca_3B_4O_{12}$-Nd^{3+} (Ln= La, Gd, Y) crystals, oriented along the crystallografic axes. Preliminary spectroscopic studies of the $La_2Ca_3B_4O_{12}$-Nd (Ln=La, Gd, Y) [10] demonstrated that the absorption and luminescence spectra show wide structureless bands with an intense host absorption in the UV. Due to considerable inhomogeneous broadening of the neodymium lines caused by the structural disordering in the La, Ca sites, the analysis of the Stark structure was highly complicated, so that we confined ourselves to analyzing the integrated characteristics of the multiplet transitions.

Experimental integrated oscillator strengths $f_{i,j}$ and the cross sections $\sigma_{i,j}$ of transitions from the ground state i to the excited multiplets j were determined from the absorption spectra using

$$f^3_{i,j}=\frac{mc^2}{N\pi e^2}\int K_{i,j}(\nu)d\nu=\frac{mc^2}{\pi e^2}\sigma^3_{i,j} \tag{1}$$

where m and e are the mass and the charge of an electron, c is the light velocity, $\int K_{i,j}(\nu)d\nu$ is the integrated absorption coefficient corresponding to $i\rightarrow j$ transition, N is the concentration of the active ions. Corresponding line strengths were determined by

$$S_{J,J'}=\frac{3h}{8\pi^2mc}\cdot\frac{9n}{(n^2+2)^2}\cdot\frac{1}{\nu}(2J+1)\cdot f_{J,J'}, \tag{2}$$

where n is the refractive index at the frequency ν.

To determine the oscillator strengths, the probabilities of the radiative transitions, and the branching coefficients we used the known expressions

$$f_{j,i}=\frac{g_i}{g_j}f_{i,j},\ A_{j,i}=\frac{8\pi^2e^2n^2}{mc}(\bar{\nu})^2f_{j,i},\ \beta_{j,i}=\frac{A_{j,i}}{\sum_k A_{j,k}}, \tag{3}$$

where ν is the average transition frequency in cm^{-1}, g_i and g_j are the degeneracies of the i and j terms. The radiative lifetimes were obtained from the total radiative transition probabilities of the $^4F_{3/2}$ neodymium term

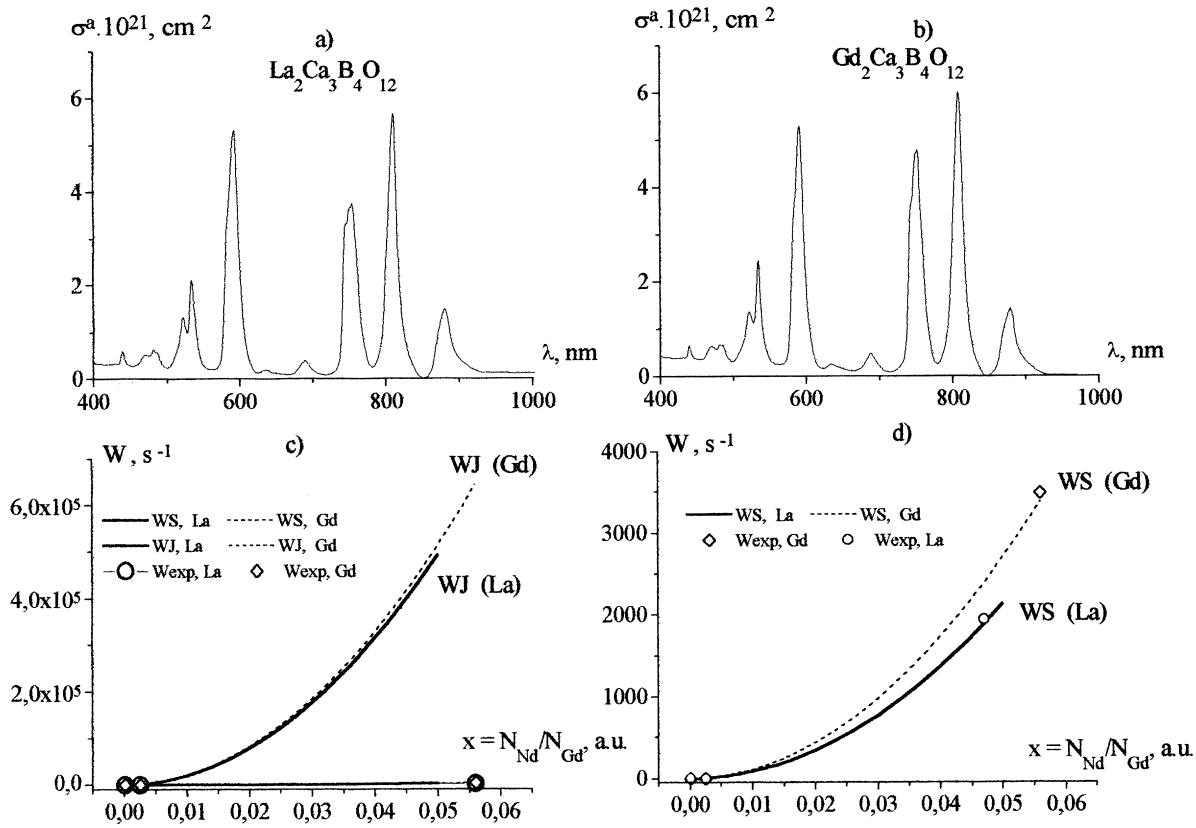

Fig. 1. Absorption cross section (a,b) and concentration dependences of selfquenching rates (c,d) in $La_2Ca_3B_4O_{12}$:Nd and $Gd_2Ca_3B_4O_{12}$:Nd crystals. W_J and W_S-selfquenching rates, calculated in hopping and static models, respectively, W_{exp}-experimental values.

$$\tau_{ИЗЛ} = \left(\sum_k A_{jk}\right)^{-1} \tag{4}$$

Calculated characteristics of the spontaneous radiative transitions were found by the standard Judd–Ofelt technique [11,12]. The oscillator strength of the electro-dipole transition in the $4f_n$ configuration can be written as

$$f_{ij}^T = \frac{8\pi^2 mc\nu\chi}{3h(2J+1)n^2} \sum_t \Omega_t \left|\langle |SL|J\|U^{(t)}\|S'L'|J\rangle\right|, \tag{5}$$

where $|\langle |SL|J\|U^{(t)}\|S'L'|J\rangle|$ are the matrix elements of the unit tensor operators, $\chi = n(n^2+^2)2/9$ for the dipole transition. Experimental oscillator strengths of the electro-dipole transitions were found from $f^{ed} = f^{exp} - f^{md}$. Oscillator strengths of the magnito-dipole transitions were taken from [13]. Setting equal the experimental and calculated oscillator strengths $f_{ij}^T = f_{ij}^{exp}$ and solving Eq. (4) by the least-square method one can find the intensity parameters Ω_t.Knowing these intensity parameters, we calculated the oscillator strengths of the absorption bands. Calculated radiative transition probabilities were obtained by

$$A_{ji}^T([S'L']J', [SL]J) = \frac{8\pi^2 e^2 \nu_{ji}^2 n^2}{mc} \frac{(2J+1)}{(2J+1)} f_{ji}^T([SL]J, [S'L']J') \tag{6}$$

Line strengths S_{ij} corresponding to transitions i–j between the excited i and j multiplets were determined by the intensity parameters W_t and transition matrix elements

$$S = \sum_t \Omega_t |\langle J|U^{(t)}|J'\rangle|^2 . \tag{7}$$

The integrated emission cross sections, radiative lifetimes of neodymium ions, and branching coefficients were calculated with f_{ij}^T and A_{ji}^T using Eq. (2). Table 1

Spectra of the absorption cross sections in the $La_2Ca_3B_4O_{12}$: Nd and $Gd_2Ca_3B_4O_{12}$: Nd crystals are shown in Figs. 1 and 1b. All crystals show absorption band at 805 nm ascribed to transition $^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$, which matches the emission spectrum of laser diode and considerably exceeds the width of the radiation spectrum of the multimode laser diodes (3–5 nm). The peak cross section of this band has maximum $\sigma^p = 5.67\times10^{-20}$ cm^2 at 806 nm in $La_2Ca_3B_4O_{12}$: Nd and $\sigma^p = 5.67\times10^{-20}$ cm^2 at 804 nm in $Gd_2Ca_3B_4O_{12}$: Nd. The maxima of the

Table 1
Intensity parameters in the $La_2Ca_3B_4O_{12}$-Nd and $Gd_2Ca_3B_4O_{12}$-Nd

Crystal	$\Omega_2\times10^{20}$, cm^2	$\Omega_4\times10^{20}$, cm^2	$\Omega_6\times10^{20}$, cm^2
$La_2Ca_3B_4O_{12}$-Nd	4.56	7.29	9.87
$Gd_2Ca_3B_4O_{12}$-Nd	4.59	7.56	10.76

Table 2
Experimental and calculated characteristics of the radiative spontaneous transitions in $La_2Ca_3B_4O_{12}$-Nd

Transition	ν, cm^{-1}	f_{ji}, 10^{-6}	A_{ji}, s^{-1}	β_{ji}	τ_{rad}, μs	τ^{exp}, μs
$^4F_{3/2} \Rightarrow {}^4I_{15/2}$	5400	0.652	39.60	0.005		
$^4F_{3/2} \Rightarrow {}^4I_{13/2}$	7500	6.972	816.76	0.10	126.7	83
$^4F_{3/2} \Rightarrow {}^4I_{11/2}$	9500	21.367	4015.94	0.509		
$^4F_{3/2} \Rightarrow {}^4I_{9/2}$	11350	11.258	3020.49	0.383		

Table 3
Experimental and calculated characteristics of the radiative spontaneous transitions of neodymium ion in $Gd_2Ca_3B_4O_{12}$-Nd

Transition	ν, cm^{-1}	f_{ji}, 10^{-6}	A_{ji}, s^{-1}	β_{ji}	τ_{rad}, μs	τ^{exp}, μs
$^4F_{3/2} \Rightarrow {}^4I_{15/2}$	5400	0.711	43.17	0.005		
$^4F_{3/2} \Rightarrow {}^4I_{13/2}$	7500	7.601	890.38	0.105	118	77.5
$^4F_{3/2} \Rightarrow {}^4I_{11/2}$	9500	23.059	4334.03	0.515		
$^4F_{3/2} \Rightarrow {}^4I_{9/2}$	11 350	11.824	3172.13	0.376		

emission spectra locate in the 1060 nm range [10]. Calculated and experimental lifetimes of the radiative transitions measured from the luminescence decay curves in samples with the neodymium concentration 1×10^{19} cm^{-3} are given in Tables 2 and 3. The line intensities in the absorption spectra are proportional to the neodymium concentration.

As is seen in Tables 2 and 3, the maximal branching coefficients $\beta=0.509$ and $\beta=0.515$ are observed for the $^4F_{3/2}-{}^4I_{11/2}$ transition, β, τ_{rad}, and τ_{exp} being somewhat higher in $Gd_2Ca_3B_4O_{12}$-Nd. Deviations between τ_{rad} and τ_{exp} are, probably, due to the non-radiative quenching of the $^4F_{3/2}$ terms by interaction with ligands. The luminescence concentration quenching in studied crystals is weak. The neodymium selfquenching microparameters and macrorates in $La_2Ca_3B_4O_{12}$-Nd and $Gd_2Ca_3B_4O_{12}$-Nd crystals estimated by the model quantum-mechanical calculation [14] showed that in $La_2Ca_3B_4O_{12}$-Nd and $Gd_2Ca_3B_4O_{12}$-Nd the migration microparameters CDD are, respectively, 6.7×10^{-38} and 6.3×10^{-38} cm^6s^{-1} and exceed the selfquenching microparameters $C_{DA}=1.3\times10^{-38}$ and 1.5×10^{-38} cm^6s^{-1}. Therefore, the neodymium selfquenching could be described within the framework of the migration limited model. But the concentration dependences of selfquenching rates (Fig. 1c Fig. 1d) show the static model. Evidently, the structural peculiarities of the studied crystals demand non-uniform distribution of the neodymium ions in the crystal. Non-uniform substitution of cation sites by neodymium ions decreases the migration rate, so that selfquenching shows the static behaviour.

4. Conclusion

According to their spectral luminescence and kinetic properties, the studied crystals of a new family of the single crystal materials on the mixed borates $Ln_2Ca_3B_4O_{12}$-Nd (Ln=La, Gd, Y) are of a great interest as new IR phosphors characterized by wide absorption and luminescence bands and weak selfquenching. These facts make such crystals possible active media for the pulse-lamp and laser-diode pumped solid-state lasers tuneable within the luminescence linewidth.

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