ELSEVIER

Journal of Alloys and Compounds 323–324 (2001) 214–217

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Optical transitions of Pr^{3+} ions in $Ca_4GdO(BO_3)_3$ crystals

M. Malinowski[a], M. Kowalska[a], R. Piramidowicz[a], T. Lukasiewicz[b], M. Swirkowicz[b],
A. Majchrowski[c,]*

[a]*Institute of Microelectronics and Optoelectronics PW, ul. Koszykowa 75, 00-662 Warsaw, Poland*
[b]*Institute of Electronic Materials Technology, ul. Wólczyñska 133, 01-919 Warsaw, Poland*
[c]*Institute of Applied Physics WAT, ul. Kaliskiego 2, 00-908 Warsaw, Poland*

Abstract

Optical properties of Pr^{3+} ions in gadolinium calcium oxoborate $Ca_4GdO(BO_3)_3$ (GdCOB) nonlinear crystals have been studied. Polarized absorption and emission spectra and fluorescence lifetime measurements have been performed and discussed using modified Judd-Ofelt theory. The system is characterized by intense red emission at 610 nm corresponding to the $^1D_2 \rightarrow {}^3H_4$ transition, no emission from the excited $^3P_0$ state has been observed. $^1D_2$ emission has been investigated under pulsed excitation and the experimental lifetimes for this level has been compared with this obtained theoretically by using Judd–Ofelt approach.

Keywords: Praseodymium; Oxoborates; GdCOB:Pr^{3+}; Luminescence; Nonlinear material

1. Introduction

Gadolinium calcium oxoborate crystals $Ca_4GdO(BO_3)_3$ (abbreviated GdCOB) doped with lanthanide ions have been recently investigated as potential nonlinear laser systems [1,2]. Such systems can give rise to short wavelength laser radiation by self frequency doubling (SFD). Neodymium and ytterbium doped GdCOB was shown to have good lasing properties and SFD in this material has been demonstrated [3–6]. Similar properties were also found in $YAl_3(BO_3)_4$ and $LiNbO_3$ crystals.

Trivalent praseodymium ion (Pr^{3+}) in various crystals is well known for having a very rich emission spectrum extending from the ultraviolet (UV) to infrared (IR) [7]. Because of the energy level structure, and suitable lifetimes of the excited states, Pr^{3+} systems are also attractive as short wavelength up-conversion laser materials [8]. Recently, simultaneous blue and orange wavelength lasing in Pr^{3+} doped YAG, YAP and YLF crystals has been reported [9] and observation of lasing at 486 nm in Pr^{3+}:GGG has been observed. This encouraged us to study spectroscopic properties of Pr^{3+} ion in $Ca_4GdO(BO_3)_3$. In this work we present Judd–Ofelt [10,11] analysis of the Pr^{3+} ion oscillator strengths in GdCOB and report on absorption, emission, and lifetime measurements in this system.

2. Experimental methods

Gadolinium calcium oxoborate, $Ca_4GdO(BO_3)_3$ (GdCOB) has the monoclinic noncentrosymmetric structure with two molecules per unit cell and space group symmetry C_m. The rare earth ions are expected to enter the lattice at gadolinium sites which are sixfold coordinated by oxygen ions and have low C_s point symmetry, the shortest Gd–Gd distance is 3.557 Å [12]. Optically, GdCOB is a biaxial crystal, optical Y axis coincides with the b crystallographic axis, while X and Y axes are at angles of 26° and 15° with respect to a and c directions, respectively, and the monoclinic β angle is 101.26° [2].

Three samples of Pr^{3+}:GdCOB with nominal concentrations of 0.3, 1 and 6 at.% of Pr^{3+}, were grown by the Czochralski method at ITME laboratory in Warsaw [13]. For the spectroscopic investigations, the samples were oriented, cut and polished in form of cubes having faces

---

*Corresponding author. Tel.: +48-22-683-9487; fax: +48-22-683-9109.

E-mail address: amajchrowski@altair.geo.wat.waw.pl (A. Majchrowski).

0925-8388/01/$ – see front matter
PII: S0925-8388(01)01113-6

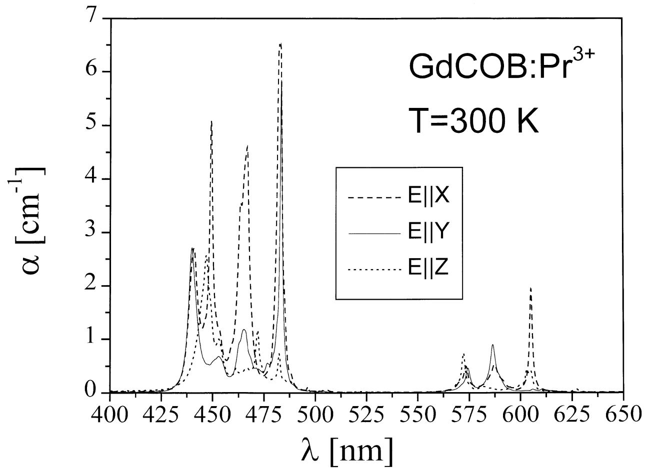

Fig. 1. Visible polarized absorption spectrum of 6 at.% Pr^{3+}:GdCOB crystal measured at room temperature.

perpendicular to the principal optical axes. The experimental apparatus used to investigate spectroscopic properties of Pr^3 ion in GdCOB has been described previously [14].

3. Results

3.1. Absorption and emission spectra

Room temperature polarized absorption spectra of 6% Pr^{3+} doped GdCOB in the 400–650 nm and 800–2600 nm ranges are presented in Figs. 1 and 2, respectively. Two groups of lines, characteristic for $4f^2 \rightarrow 4f^2$ transitions of trivalent praseodymium, located in the blue and orange range, which corresponds to the $^3H_4 \rightarrow {}^3P_0$ and $^1D_2$ transitions respectively, could be observed. $^1I_6$ Stark levels, which are forbidden by the spin selection rules for one-photon absorption transitions from the $^3H_4$ ground state are weak and could not be identified. Below about 300 nm the background absorption of the host crystal begins to increase and it grows rapidly at about 250 nm. From Figs. 1 and 2 it is seen that Pr^{3+}:GdCOB spectra are strongly polarization dependent, with EIIX polarization giving the strongest absorption.

After excitation with blue, 476 nm line of an argon laser, emission of the crystals was recorded between 300 nm and 2 μm. Fig. 3 illustrates the room temperature emission spectrum of 1% Pr^{3+}:GdCOB in the visible range. As can be seen, after blue excitation GdCOB fluorescence is dominated by the transitions from the excited $^1D_2$ state, populated by the non-radiative relaxation from the $^3P_0$ state. However, contrary to most praseodymium systems [7–9] no fluorescence originating from the $^3P_0$ has been observed in GdCOB. The determination of individual Stark levels of the Pr^{3+} ions in GdCOB was made by us by analyzing various low temperature absorption, excitation and dye laser selectively excited $^1D_2$ emission spectra which showed well resolved, sharp lines.

3.2. Optical transition intensity analysis

Once the energy levels have been determined, the Judd–Ofelt [10,11] intensity analysis was performed using the *X*, *Y* and *Z* polarized absorption spectra as proposed. It is known, that there are problems in describing the intensity of praseodymium transitions by the Judd–Ofelt theory due to the low lying 5d level which contributes to the oscillator strength of the 4f transitions. Thus, to account for the mixing of the lowest 4f5d state with the 4f^2 states of Pr^{3+} we have used modification proposed by Dunina et al. [15]. Since the details of the Judd–Ofelt theory, its precision and drawbacks have been extensively analyzed elsewhere [15–17] we have presented here only the essential results. The central main result of the Judd–Ofelt theory is that the oscillator strength $f_{\mathrm{calc.}}$ of an electric dipole transition

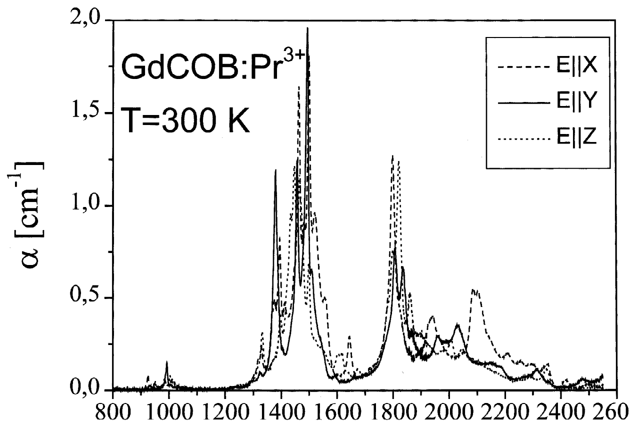

Fig. 2. Infra-red polarized absorption spectrum of 6 at.% Pr^{3+}:GdCOB crystal measured at room temperature.

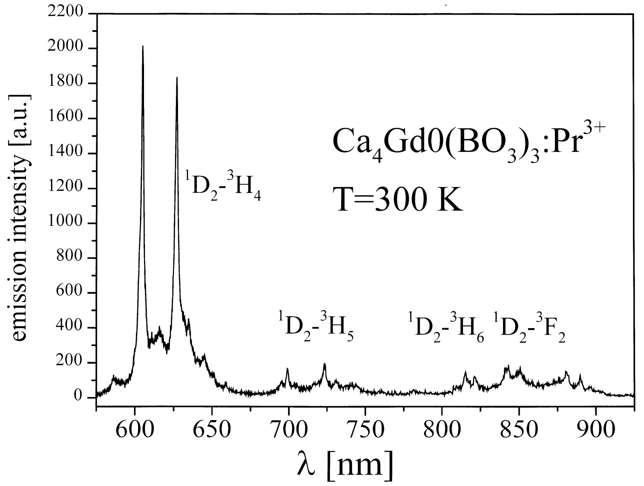

Fig. 3. Room temperature visible emission spectrum of 1 at.% Pr^{3+}:GdCOB crystal excited at 476 nm by argon laser.

Table 1
Measured and calculated polarized oscillator strengths for Pr^{3+} ion in $Ca_4GdO(BO_3)_3$

Polarization: absorption transitions $^3H_4 \rightarrow$	$E\|X$			$E\|Y$			$E\|Z$		
	λ [nm]	$f_{exp.}$ [$\times 10^{-7}$]	$f_{calc.}$ [$\times 10^{-7}$]	λ [nm]	$f_{exp.}$ [$\times 10^{-7}$]	$f_{calc.}$ [$\times 10^{-7}$]	λ [nm]	$f_{exp.}$ [$\times 10^{-7}$]	$f_{calc.}$ [$\times 10^{-7}$]
$^3H_6$	2284	6.65	2.05	2269	4.90	1.59	2256	4.32	1.52
$^3F_2$	1865	11.61	11.50	1853	9.93	9.89	1830	12.16	12.40
$^3F_3$	1557	24.49	25.60	1553	17.13	17.80	1656	18.76	15.90
$^3F_4$	1305	8.17	10.80	1301	8.27	10.10	1306	5.45	10.80
$^1G_4$	1016	2.11	0.64	992.3	1.43	0.52	975.8	2.16	0.53
$^1D_2$	587.5	15.10	6.72	588.07	10.50	5.02	591.1	9.40	4.69
$^3P_0$	482.2	49.13	54.90	483.17	30.41	25.00	490.2	7.18	12.50
$^3P_1$	465.47	62.75	57.50	466.12	20.80	26.20	467.8	17.35	13.30

Table 2
Intensity parameters for Pr^{3+} ion in $Ca_4GdO(BO_3)_3$

Polarization	Ω_2 [$\times 10^{-20}cm^2$]	Ω_4 [$\times 10^{-20}cm^2$]	Ω_6 [$\times 10^{-20}cm^2$]	RMS [$\times 10^{-7}$]
$E\|X$	−2.230	7.892	1.912	5.21
$E\|Y$	0.472	3.526	2.030	4.16
$E\|Z$	2.637	1.790	2.277	4.34
$\Omega_{effective}$ [$\times 10^{-20}cm^2$]	0.879	13.208	6.219	

between rare-earth ion multiplets ($J \rightarrow J'$) can be expressed by

$$f_{calc.}(aJ,bJ') = \frac{8\pi^2 m\nu}{3h(2J+1)n^2}\chi \sum_{t=2,4,6} \left| \left\langle 4f^n|a,J\|U^{(t)}\|4f^n|b,J' \right\rangle \right|^2 \left(1 + \frac{E(J)+E(J')-2E(4f)}{E(5d)-E(4f)}\right) \quad (1)$$

where h is Planck's constant, J is the angular momentum of the initial level, $\chi = n(n^2+2)^2/9$ is a local field correction factor, $\langle a\|U^{(t)}\|b\rangle$ are the doubly reduced matrix elements and Ω_t are empirically determined parameters. The last term in Eq. (1) expresses the modification made by Dunina et al. [15]. Here $E(J)$, $E(J')$ and E(5d) are the energies of the initial state, final state, and lowest 4f5d state respectively, and E(4f) is the average energy over the 4f configuration. Using the values of the experimentally measured oscillator strength $f_{exp.}$ the three intensity Ω_t parameters were evaluated from the least-square fit of measured $f_{exp.}$ and calculated $f_{calc.}$ oscillator strengths. Table 1 shows the average wavelengths for the analyzed transitions together with the measured $f_{exp.}$ and calculated $f_{calc.}$ oscillator strengths for all measured absorption transitions. The resulting set of Judd–Ofelt parameters was found to be; $\Omega_2 = 0.879\ 10^{-20}$ cm^2, $\Omega_4 = 13.208\ 10^{-20}$ cm^2, $\Omega_6 = 6.219\ 10^{-20}$ cm^2, see Table 2. A measure of the quality of the fit can be evaluated from the RMS deviation between the measured and calculated oscillator strengths values. The RMS deviation of the order of 0.5×10^{-6} is lower than values often found by applying Judd–Ofelt theory to Pr^{3+} ion in other systems [18]. From the determined set of Ω_t intensity parameters the electric dipole transition probabilities A(aJ,bJ′) from the excited $^1D_2$ state to lower lying states, together with the resulting branching ratios $\beta_{calc.}$ were calculated and are given in Table 3. The experimental values of branching ratios $\beta_{exp.}$ were also obtained from the non polarized fluorescence spectra by comparing relative areas under the emission peaks and are listed in the last column of Table 3. It can be seen that the highest calculated value of the branching ratio is for the $^1D_2 \rightarrow {}^3H_4$ transition which is found to be in reasonable agreement with the experimentally determined value.

Radiative lifetimes of the $^3P_0$ and $^1D_2$ were calculated to be 10.7 and 193.1 μs, respectively and are comparable in magnitude to values found in other praseodymium doped oxide crystals [18].

Table 3
Calculated radiative transition probabilities and branching ratios for the $^1D_2$ level of Pr^{3+} ion in $Ca_4GdO(BO_3)_3$

Transition $^1D_2 \rightarrow$	λ [nm]	A_{ij} [s^{-1}]	β_{calc} [%]	β_{exp} [%]
$^1G_4$	1497.90	291.10	5.62	5.6
$^3F_4$	1035.51	384.54	7.43	7.4
$^3F_3$	963.57	191.69	3.70	2
$^3F_2$	856.53	1211.08	23.38	14
$^3H_6$	810.43	1174.36	22.67	19
$^3H_5$	697.93	54.01	1.04	4
$^3H_4$	587.99	1871.87	36.14	48
τ_{rad} [μs]		193.10		

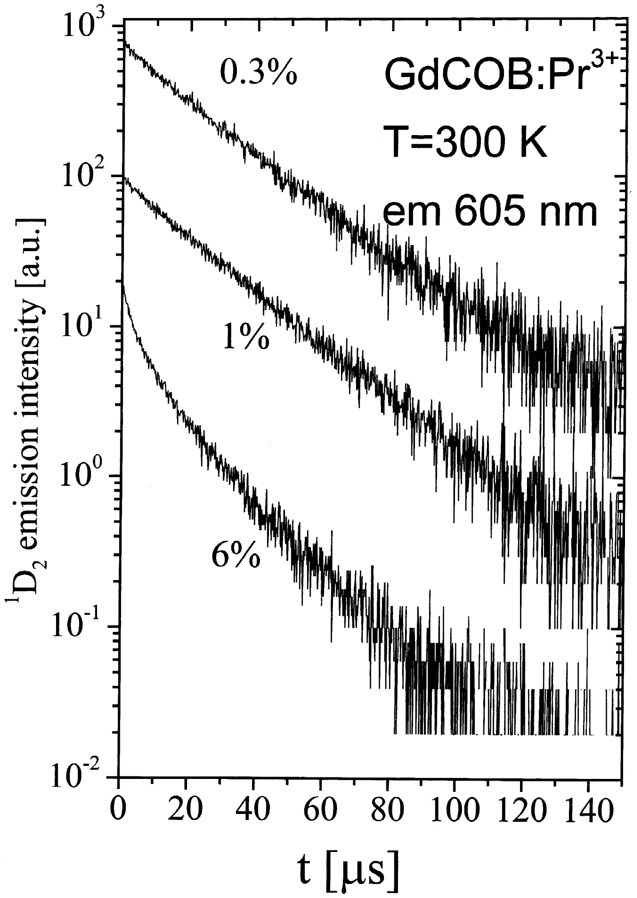

Fig. 4. Red fluorescence decay at 605 nm corresponding to the $^1D_2 \rightarrow {}^3H_4$ transition of Pr^{3+}:GdCOB crystal measured at 300 K for different concentrations of activator.

3.3. Fluorescence dynamics

Fig. 4 shows the decay profiles of the $^1D_2$ level measured at room temperature. In 0.3% and 1% Pr^{3+} doped samples these decays are exponential with time constants of about 27 μs, in 6% Pr^{3+} crystal fluorescence decay was non-exponential and much faster. This is an indication of cross relaxation by energy transfer among Pr^{3+} ions. The lifetime observed in 0.3% Pr^{3+} sample is much shorter than the calculated $^1D_2$ radiative lifetime, suggesting its predominantly nonradiative character. From the comparison of the radiative and measured lifetime values nonradiative transition probability W_{NR} for the energy gap between the lowest $^1D_2$ Stark energy level and the next lower lying level in $^1G_4$ multiplet of 5842 cm^{-1} is calculated to be 3328 s^{-1}. Also the absence of the $^3P_0$ emission and the lack of rise time in the decay profile of the $^1D_2$ emission after excitation of the $^3P_0$ level could be attributed to very fast nonradiative decay of this level. This is consistent with the very high phonon cut-off energy in the borate host matrix of about 1470 cm^{-1}.

4. Conclusions

The spectroscopic properties of Pr^{3+} ion in gadolinium calcium oxoborate $Ca_4GdO(BO_3)_3$ (GdCOB) crystals were studied and analyzed. Absorption spectra have been obtained leading to the determination of Judd–Ofelt intensity parameters and radiative transition probabilities. When comparing properties of various praseodymium doped materials it is apparent that the praseodymium ion emission in GdCOB is strongly influenced by nonradiative decay. The emission from the $^3P_0$ level has not been observed and visible, red Pr^{3+} fluorescence originating from excited $^1D_2$ state presents much shorter lifetime comparing with these of praseodymium in other oxide crystals [18].

Acknowledgements

This work was partially supported by the Polish State Committee on Science (KBN) – project no. 7 T08A 008 13.

References

[1] A. Aaron, P.Y. Tigreat, A. Caramanian, E. Antic-Fidancev, B. Viana, G. Aka, D. Vivien, J. Lumin. 87–89 (2000) 611.
[2] G. Aka, A. Kahn-Harari, F. Mougel, D. Vivien, F. Salin, P. Coquelin, P. Colin, D. Pelenc, J.P. Damelet, J. Opt. Soc. Am. B14 (1997) 2238.
[3] F. Mougel, K. Dardenne, G. Aka, A. Kahn-Harari, D. Vivien, J. Opt. Soc. Am. B16 (1999) 164.
[4] F. Mougel, G. Aka, A. Kahn-Harari, H. Hubert, J.M. Benitez, D. Vivien, Opt. Mater. 8 (1997) 161.
[5] J. Lu, G. Li, J. Liu, S. Zhang, H. Chen, M. Jiang, Z. Shao, Opt. Commun. 168 (1999) 405.
[6] F. Auge, F. Balembois, P. Georges, A. Brun, F. Mougel, G. Aka, A. Kahn-Harari, D. Vivien, Appl. Opt. 38 (1999) 976.
[7] A.A. Kaminskii, Advanced Solid-State Lasers (New Orleans, MS1-3 February 1993) Vol. 15, in: A. Pinto, T.Y. Fan (Eds.), Washington DC, OSA, p. 266.
[8] D.M. Baney, G. Rankin, K. Chang, Opt. Lett. 21 (1996) 1372.
[9] M. Malinowski, M.F. Joubert, R. Mahiou, B. Jacquier, J. Phys. IV (1994) C4–C541.
[10] B.R. Judd, Phys. Rev. 127 (1962) 750.
[11] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511.
[12] R. Norrestam, M. Nygren, J.O. Bovin, Chem. Mater. 4 (1992) 737.
[13] A. Majchrowski, T. Łukasiewicz, Z. Mierczyk, E-MRS Spring Meeting, CD-ROM Proceedings, Strasbourg 1-4 June 1999, J-IV.1
[14] M. Malinowski, R. Piramidowicz, J. Sarnecki, W. Woliñski, J. Phys.: Condens. Matter 10 (1998) 1909.
[15] E.B. Dunina, A.A. Kaminskii, A.A. Kornienko, K. Kurbanov, K.K. Pukhov, Sov. Phys. Solid State 32 (1990) 920.
[16] A.A. Kaminskii, E.L. Belokoneva, B.V. Mill, S.E. Sarkisov, K. Kurbanov, Phys. Stat. Solidi (a) 97 (1986) 279.
[17] W.F. Krupke, Phys. Rev. 145 (1966) 325.
[18] C. Gorller-Walrand, K. Binnemans, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earth, Vol. 25, Elsevier, Amsterdam, 1998, p. 101.