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Growth and optical properties of Pr^{3+}:$La_2CaB_{10}O_{19}$ crystal

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Abstract: Pr^{3+} doped $La_2CaB_{10}O_{19}$ crystal were grown by the top-seeded solution growth (TSSG) method. The absorption spectra, emission spectra and lifetime were measured at room temperature. The J-O parameters (Ω_t, t=2,4,6), the radiative transition probabilities $A_{J,J'}$, oscillator strengths $P_{J,J'}$, radiative lifetime τ, fluorescence branch ratios β_J and the value of integrated emission cross section have also been calculated. Five main absorption bands, $^3H_4$ to $^3P_1$+$^3P_2$, $^3P_0$, $^1D_2$, $^3F_3$ + $^3F_4$ and $^3F_2$, were observed in the absorption spectra. The $^1G_4$ absorption band was not observed. A very strong emission band at 601 nm ($^1D_2 \rightarrow {}^3H_4$) was observed in the emission spectra. The experimental lifetime for this level was compared with that obtained theoretically by using J-O approach.

Keywords: Pr^{3+}:$La_2CaB_{10}O_{19}$ crystal; crystal growth; spectroscopic properties; rare earths

Trivalent praseodymium ion doped systems, showing rich emission spectrum which extends from IR, through visible, up to UV range, have been extensively studied[1]. 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[2]. Recently, simultaneous blue and orange wavelength lasing in Pr^{3+} doped YAG, YAP and YLF crystals have been reported[3], and lasing at 486 nm in Pr:GGG has been observed[4]. Q-switching and mode-locking have been achieved in a flashlamp pumped Pr:YLF laser[5]. In addition, the first demonstration of femtosecond pulse generation in a visible solid-state laser, mode locked by the KLM technique, has been reported in Pr:YLF crystal[6,7].

As a potential nonlinear laser crystal, $La_2CaB_{10}O_{19}$ (abbreviated as LCB) doped with lanthanide ions, such as Nd^{3+}, Yb^{3+} and Er^{3+} ions, have been investigated[8–13]. These crystals exhibit excellent spectroscopic and laser properties. Neodymium doped LCB shows lasing properties and SFD in this material has been demonstrated[14,15]. In this work, we presented modified Judd-Ofelt[16–18] analysis of the Pr^{3+} ion oscillator strengths in LCB, and also reported the absorption, emission, and lifetime measurements in this system.

1 Crystal growth

Pr:$La_2CaB_{10}O_{19}$ crystals were grown by the top-seeded solution growth (TSSG) method in CaO-Li_2O-B_2O_3 flux system at about 980 °C. The crystal growth conditions were similar to those of $La_2CaB_{10}O_{19}$ crystals, as reported in Refs. [19–21]. A yellow crystal was obtained, and a (010) slice of 1 mm thickness was cut from the crystal and polished, as shown in Fig. 1. Scattering centers were observed in the slice when it was illuminated with a 150 mW green laser, as shown in Fig. 2. The centers may be caused by solvent inclusions. To make improvement on crystals quality, slower growth rates and a decent temperature gradient are required[22].

The content of Pr^{3+} ions in Pr:LCB crystal was determined by ICP-AES method to be 0.99×10^{20} ions/cm^3, and

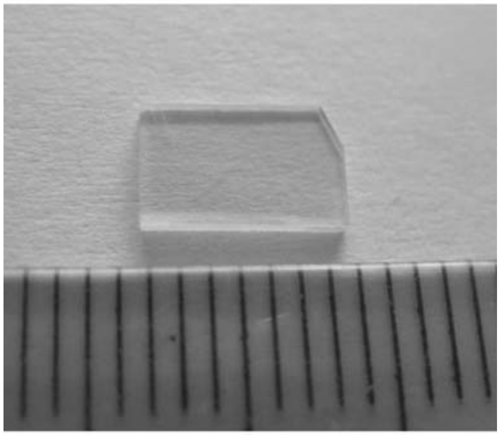

Fig. 1 Pr:LCB crystal sample

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the segregation coefficient was calculated to be 0.63. It is a little higher than that in Nd: $La_2CaB_{10}O_{19}$ crystals.

2 Spectroscopic properties

The absorption spectrum was measured on a Lambda-900 UV-VIS-NIR spectrophotometer at room temperature. Fig. 3 shows the absorption spectrum of Pr:LCB crystal in the range from 300 to 2500 nm. Five main absorption bands at 436, 489, 578, 1484 and 1874 nm are observed, which correspond to the transitions from $^3H_4$ to $^3P_1$+$^3P_2$, $^3P_0$, $^1D_2$, $^3F_3$+$^3F_4$ and $^3F_2$, respectively. The $^1G_4$ absorption band was not observed maybe because of the strong background absorption. All the transitions are assigned[23] and marked in Fig. 3.

There are problems in describing the intensity of praseodymium transitions by using the Judd-Ofelt theory due to the low lying 5d level which contributes to the oscillator strength of the 4f transitions. Therefore, we used the modified Judd- Ofelt (J-O) theory[16–18] to characterize the optical parameters of f-f transitions of Pr^{3+} in Pr:LCB crystal. The calculated spectral parameters are listed in Table 1. According to the modified J-O theory, the calculated absorption line strengths S_{cal} can be expressed in terms of J-O parameter $\Omega_{2,4,6}$ as

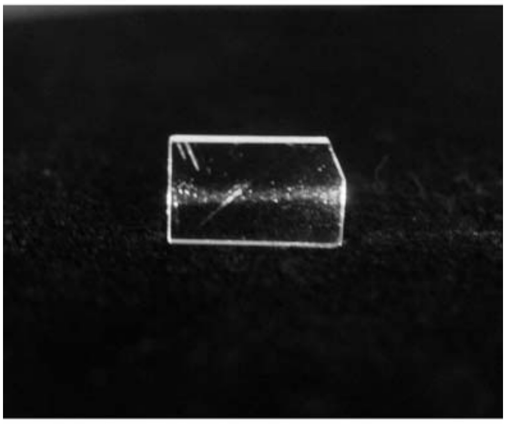

Fig. 2 Optical scattering centers in the crystal

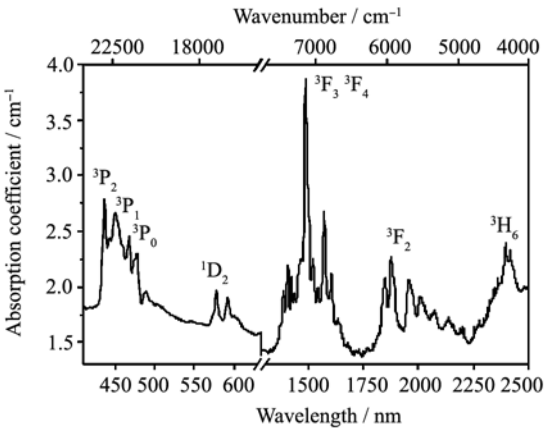

Fig. 3 Absorption spectrum of Pr:LCB crystal at 300 K

$$S_{JJ'}=\sum_{t=2,4,6}\Omega_t[1+2\alpha(Ej+Ej'-2E_f^0)]\times\left|\left\langle\Phi J\left\|U^{(t)}\right\|\Phi'J'\right\rangle\right|^2 \quad (1)$$

where Ω_t are the modified J-O parameters, α is an additional parameter with a value of about 10^{-5} cm^{-1} for Pr^{3+}[18]. The reduced tensor matrix elements $|<\Phi J||U^{(t)}||\Phi'J'>|^2$ are almost independent of the host environment and the values of the matrix elements are taken as those reported by Carnall et al.[23] A least-squares fitting provided the values of the three J-O parameters: Ω_2=6.23×10^{-20} cm^2, Ω_4=1.87×10^{-19} cm^2, Ω_6=1.36×10^{-19} cm^2. The ΔS_{rms} deviation between the experimental and calculated line strengths values is 2.724×10^{-20} cm^{-2}, which is useful to evaluate the quality of the fit.

From the determined set of Ω_t intensity parameters the radiative transition rate $A(J\to J')$[24] for the electric-dipole transitions from the excited levels located below the $^3P_1$ level were calculated and are given in Table 2. The values of

Table 1 Measured and calculated line strengths of Pr^{3+} in LCB crystal

J manifold	$\bar{\lambda}$/ nm	$S_{exp.}$/ (10^{-20} cm^2)	$S_{cal.}$/ (10^{-20} cm^2)	$\sigma_{abs}(\lambda)$/ (10^{-20} cm^2)
$^3P_2$,$^3P_1$	436	8.0381	5.7269	1.4461
$^3P_0$	489	4.2957	3.2389	0.6020
$^1D_2$	578	2.7682	1.0443	0.6213
$^3F_3$, $^3F_4$	1484	25.7067	24.107	2.5436
$^3F_2$	1874	14.0213	12.3330	0.9239

Table 2 Luminescence parameters of Pr^{3+} in LCB crystal

Radiation transition	λ/ μm	P_{ed}/ 10^{-6}	$A(J''\to J')$/ s^{-1}	$\tau_{rad.}$/ μs	$\beta_{J'}$/ %	$\Sigma(J''\to J')$/ (10^{-18} cm)
$^3P_0\to{}^1D_2$	2.946	0.453	9.23	7.23	0.006	0.401
$\to{}^1G_4$	0.945	13.957	2902		2.091	12.339
$\to{}^3F_4$	0.740	51.035	17399		12.61	45.119
$\to{}^3F_2$	0.654	46.709	20502		14.811	41.295
$\to{}^3H_6$	0.624	26.446	12744		9.211	23.381
$\to{}^3H_4$	0.494	109.109	84811		61.293	96.463
$^1D_2\to{}^1G_4$	1.392	10.598	1007	101	10.174	9.369
$\to{}^3F_4$	0.989	11.411	2165		21.868	10.089
$\to{}^3F_3$	0.936	1.776	376.7		3.804	1.569
$\to{}^3F_2$	0.840	6.344	1674		16.908	5.609
$\to{}^3H_6$	0.792	5.428	1613		16.288	4.799
$\to{}^3H_5$	0.681	0.201	80.99		0.8178	0.177
$\to{}^3H_4$	0.594	5.589	2984		30.138	4.942
$^3P_1\to{}^1D_2$	2.457	1.024	30.46	7.44	0.023	0.905
$\to{}^1G_4$	0.888	7.045	1661		1.236	6.229
$\to{}^3F_4$	0.705	42.027	15820		11.771	37.156
$\to{}^3F_3$	0.678	59.283	24188		17.996	52.412
$\to{}^3F_2$	0.626	14.917	7149		5.319	13.188
$\to{}^3H_6$	0.599	15.789	8277		6.158	13.959
$\to{}^3H_5$	0.533	68.850	45832		34.099	60.869
$\to{}^3H_4$	0.478	37.814	31448		23.397	33.431

the integrated emission cross section, the branching ratios β_J of each of the transitions as well as the total radiative lifetime τ of each of the excited levels are also collected in Table 2. From the luminescence parameters of the crystal listed in Table 2, we can see that the radiative lifetime of levels $^3P_0$, $^1D_2$ and $^3P_1$ are 7.23, 101 and 7.44 μs, respectively, which are comparable to values in Pr^{3+} doped $Ca_4GdO(BO_3)_3$ crystals[25]. The branching ratios for the transitions $^1D_2 \rightarrow {}^3H_4$ and $^1D_2 \rightarrow {}^3F_4$ were calculated to be 30.1% and 21.9%, respectively.

Excited by 488 nm line of an argon laser at room temperature, emission of the crystal was recorded from 500 nm to 900 nm, as shown in Fig. 4. A very strong emission band at 601 nm ($^1D_2 \rightarrow {}^3H_4$) and four weak emission bands at 496 nm ($^3P_0 \rightarrow {}^3H_4$), 535 nm ($^3P_0 \rightarrow {}^3H_5$), 702 nm ($^1D_2 \rightarrow {}^3H_5$) and 816 nm ($^1D_2 \rightarrow {}^3H_6$) were observed in the spectra. The FWHM of the strongest emission band was 17.96 nm. The fluorescence lifetime decay curve at 601.2 nm of the crystal was measured on a FLS920 Edinburgh Instruments spectrophotometer, as shown in Fig. 5. The fluorescence lifetime τ_f was derived as 21.95 μs, so the radiative quantum efficiency $\eta = \tau_f/\tau_{rad}$=22%. Due to the nonradiative character of Pr^{3+} ion in LCB, the measured fluorescence lifetime is much shorter than the calculated $^1D_2$ radiative lifetime.

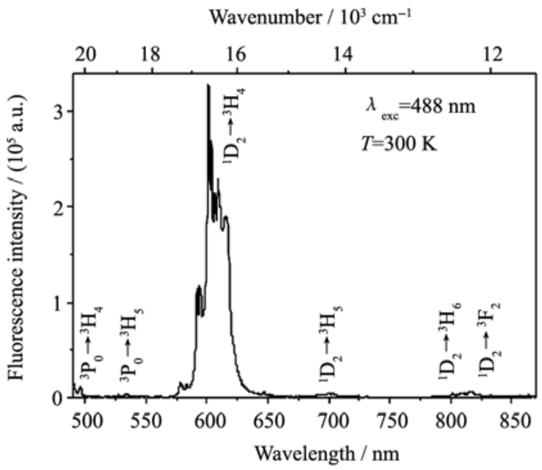

Fig. 4 Emission spectrum of Pr:LCB crystal at 300 K

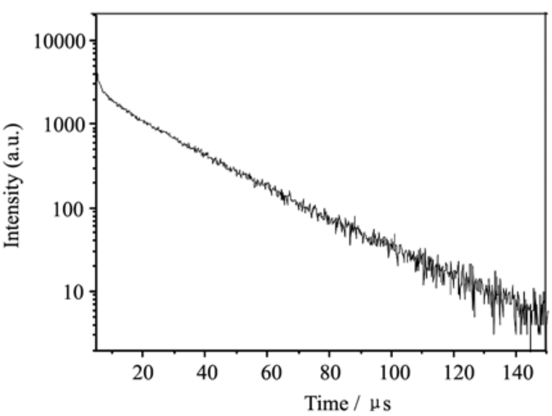

Fig. 5 Fluorescence lifetime decay curve of Pr:LCB crystal at 601.2 nm

3 Conclusions

The Pr:LCB crystal was grown by TSSG method, the absorption and emission spectra of which were investigated. The modified Judd-Ofelt theory was applied to evaluate the optical transition probabilities of Pr^{3+} ions in Pr:LCB. Based on Judd-Ofelt theory, the modified intensity parameters Ω_t obtained by the least square fitting method were Ω_2=6.23×10^{-20} cm^2, Ω_4=1.87×10^{-19} cm^2, Ω_6=1.36×10^{-19} cm^2. The measured fluorescence lifetime was 22 μs at room temperature, and the quantum efficiency was about 22%. The emission from $^1D_2$ level was so strong that the emission from $^3P_0$ level could barely be seen. The lifetime of the $^1D_2$ excited state was a little shorter compared with that of praseodymium in GdCOB crystal[25].

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