Growth and spectroscopic properties of Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal

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This paper reports the growth and spectroscopic properties of Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal. A transparent Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal with large size has been successfully grown by the Czochralski method. The spectral parameters of Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystals have been calculated and analyzed based on the Judd-Ofelt theory. The emission cross-sections, fluorescence lifetime and the fluorescence quantum efficiency of the $^1D_2$ multiplets were estimated. The investigated result regarded Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal as a potential medium for solid-state laser.

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1. Introduction

Trivalent praseodymium ion (Pr^{3+}) has rich emission spectral lines from the ultraviolet to near infrared regions. Previously the spectroscopic and laser properties of variety of Pr^{3+} ions doped materials have been investigated, such as $YAlO_3$, $LiYF_4$ [1, 2]. The Pr^{3+} lasers have a variety of applications, such as the environmental sensing, optical storage technology, underwater communications, photodynamic therapy [3, 4]. Borate crystals were attracted much attention as functional materials in laser, nonlinear optics, piezoelectricity and scintillation engineering [5, 6]. The $Sr_3La_2(BO_3)_4$ crystal belongs to the orthorhombic system with space group Pc21n [7]. The Er^{3+} and Yb^{3+}-doped $Sr_3La_2(BO_3)_4$ crystals were regarded as potential laser materials owing to its excellent chemical, physical and optical properties [8, 9]. In order to explore the more efficient Pr^{3+}-doped crystal material, this paper reports on the crystal growth and spectroscopic properties of Pr^{3+}: $Sr_3La_2(BO_3)_4$ crystal.

2. Experiment

Since $Sr_3La_2(BO_3)_4$ crystal melts congruently at about 1337°C, it can be grown by the Czochralski method. The raw materials were synthesized by the solid-state reaction method. The chemicals used were Sr_2CO_3, La_2O_3, Pr_2O_3 and H_3BO_3 with 99.99% purity. The raw materials were weighed accurately according to the stoichiometric ratio of $Sr_3La_{1.988}Pr_{0.012}(BO_3)_3$. A 3wt% excess amount of H_3BO_3 was added to compensate the loss of B_2O_3 volatilization in the process of the solid-state and growth. The weighed raw materials were ground and extruded to form pieces. Then pieces were placed in a platinum crucible and held to 1050℃ for 24 h. The process was repeated once again to assure adequate solid-state reaction. Then synthesized raw materials were melted in a ∅ 45×40 mm^3 iridium crucible. The crystal was grown in a 25 KHz frequency furnace in a N_2 atmosphere. The crystal was grown at a pulling rate of 0.6 mm h^{-1}, and a rotating rate of 15 rev min^{-1}. When growth ended, the crystal was pulled out of the melt and cooled down to room temperature at a cooling rate of 30 ℃ h^{-1}.

A high optical quality sample with dimensions of 10×6×1.32 mm^3 cut from the as-grown crystal was used for the spectral measurements. The absorption spectrum was measured at room temperature using a Perkin Elmer UV–vis–NIR Spectrometer (Lambda-900) in a range from 200 to 2300 nm wavelength. The fluorescence spectrum was measured using an Edinburgh spectrophotometer (FLS920) at room temperature. The fluorescence lifetime was measured by Lifespec-ps system of Edinburgh Instruments Ltd. The light source is continuous tunable picosecond pulsed Ti: sapphire (Tsunami+GWU). In experiment of lifetime measurement, the pulse duration of the incident light is 2~100 ps, the time resolution of the MCP-PMT detector is about 50 ps, the resolution of the monochromater is 0.5~2 nm, and the signal-to-noise ratio of Lifespec-ps system is 6000:1.

3. Results and discussions

3.1 Crystal growth

A Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal with dimensions of ϕ25×30 mm^3 was successfully grown by the Czochralski method. The grown crystal is transparent and free crack, as shown in Fig. 1. The concentration of Pr^{3+} ions in the grown crystal was measured to be 0. 364×10^{20} ions cm^{-3} (0.49 at. %) by ICP atomic emission spectroscopy.

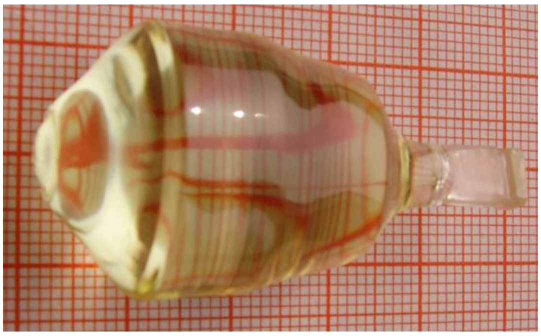

Fig. 1. Pr^{3+}:$Sr_3La_2(BO_3)_4$ single crystal grown by the Czochralski method.

3.2 Absorption spectroscopy and Judd-Ofelt analysis

Fig. 2 shows the absorption spectrum of Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal at the room temperature. These sharp absorption lines were assigned to transitions from the $^3H_4$ ground state manifold to the excited manifolds of Pr^3+ ions. The strongest Pr^{3+} absorption band was centered at 449 nm and 1529 nm, corresponding to the $^3H_4$→$^3P_0$, $^3P_1$, $^1I_6$ and $^3P_2$ and $^3H_4$→$^3F_3$+$^3F_4$ transition, respectively. The absorption band at 449 nm has a full widths at half maximum (FWHM) of 15 nm and its absorption cross-section σ_{abs} was be estimated to be 1.76×10^{-20} cm^2, which can be effectively pumped by visible diode laser sources.

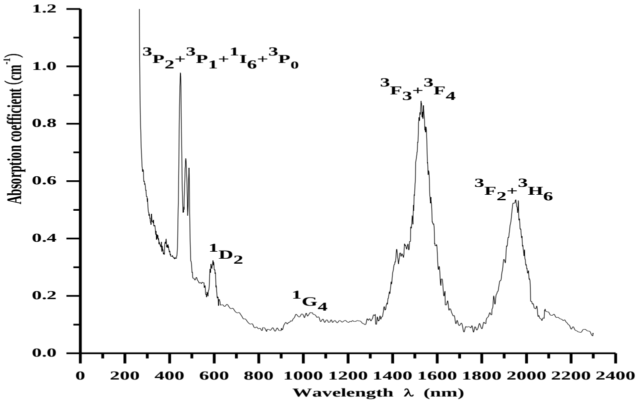

Fig. 2. Absorption spectrum of Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal at room temperature.

The standard and modified Judd–Ofelt (J-O) theories are widely used to analyze the spectroscopic properties of 4 *f* transitions of Pr^{3+} ions in various hosts [10-12]. The oscillator strength parameter, radiative transition rates, radiative lifetime and fluorescence branch ratio were calculated based on the absorption spectrum. The calculating procedures follow those described elsewhere [12], the results are listed in Table 1. The radiative lifetimes of the $^3P_0$ and $^1D_2$ multiplets are calculated to be 10.14 and 126.89 μs, respectively.

Tabel 1. The oscillator strength parameters Ω_t, radiative transition rates, fluorescence branching ratios and radiative lifetimes of Pr^{3+}: $Sr_3La_2(BO_3)_4$ crystal determined by the modified J-O theory.

Excited levels	Terminal levels	Wavelength (nm)	A(s^{-1})	β (%)	τ_f (μs)
$^3P_0$	$^1D_2$	2564	20.19	0.02	10.14
	$^1G_4$	926	2.055×10^3	2.084	
	$^3F_4$	722	1.137×10^4	11.53	
	$^3F_3$	697	0	0	
	$^3F_2$	637	2.124×10^4	21.547	
	$^3H_6$	610	2.113×10^4	21.437	
	$^3H_5$	538	0	0	
	$^3H_4$	484	4.277×10^4	43.381	
$^1D_2$	$^1G_4$	1439	1.002×10^3	12.714	126.89
	$^3F_4$	1000	1.988×10^3	25.223	
	$^3F_3$	957	197.145	2.501	
	$^3F_2$	844	869.181	11.029	
	$^3H_6$	797	867.745	11.01	
	$^3H_5$	678	45.817	0.581	
	$^3H_4$	595	2.911×10^3	36.941	
Stard.	Ω_2=-2.57, Ω_4=9.61, Ω_6=7.04; Rmserror=6.3%				
Modif.	Ω_2=4.73, Ω_4=8.46, Ω_6=16.83; Rmserror=1.7%				

3.3 Fluorescence spectra and lifetime

Fig. 3 illustrates the emission spectrum of Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal at the room temperature. In the visible region there are two intensive fluorescence bands. The emission bands centered at 551 nm is due to $^3P_0 \rightarrow {}^3H_5$ transition, the emission bands centered at 606 nm is the overlap of corresponding to $^3P_0 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3H_4$ transitions. Due to the narrow energy gap between the $^3P_0$ and $^1D_2$ multiplets (about 3600 cm^{-1}), the rate of multiphonon relaxation from $^3P_0$ to the next lower $^1D_2$ multiplet is quite high. Therefore, the fluorescence branching ratios for the $^3P_0 \rightarrow {}^1D_2$ transition is also small (about 0.02%) as showed in Table 1. In the NIR region, there are two main emission bands located around 878 and 1038 nm, corresponding to the $^1D_2 \rightarrow {}^3H_6 + {}^3F_2$ and $^1D_2 \rightarrow {}^3F_3 + {}^3F_4$ transitions, some weak emissions related to other transitions are marked in Fig. 3.

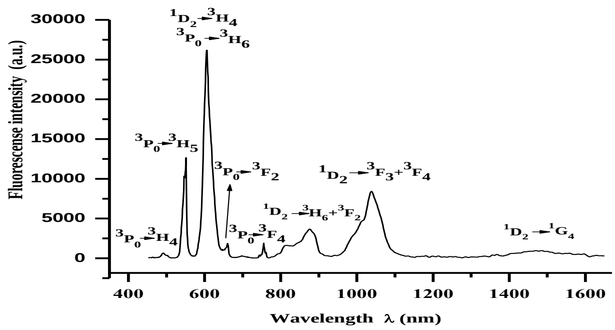

Fig. 3. Emission spectra of Pr^{3+}: $Sr_3La_2(BO_3)_4$ crystal excited 449 nm radiation at room temperature.

The $^1D_2 \rightarrow {}^3F_3 + {}^3F_4$ transition excited at 594 nm was selected to investigate the decay properties of the $^1D_2$ multiplet. The $^1D_2$ decay curve follows a single-exponential behavior. The fluorescence lifetime τ_f and quantum efficiency η of the $^1D_2$ manifold can be derived as 34.9 μs and 27.5% respectively, which are higher than those of other borate crystals, such as 21.7μs and 7.8% of Pr^{3+}:LaB_3O_6 crystal [12], 27 μs and 14% of Pr^{3+}:$Ca_4GdO(BO_3)_3$ crystal [13]. The $^3P_0 \rightarrow {}^3H_4$ transitions was selected to investigate the fluorescence lifetime of the $^3P_0$ multiplet excited at 449 nm, but no fluorescence decay curve of the $^3P_0$ multiplet was obtained. It is a reason that the fluorescence lifetime of the $^3P_0$ multiplet is too short to determine for our used instrument.

3.4 Stimulated emission cross-sections

According to the fluorescence spectrum, the stimulated emission cross-sections at various wavelengths can be estimated by the Füchtbauer-Ladenburg (F–L) formula [14]

$$\sigma_{em}(\lambda) = \frac{\lambda^5 A(J \rightarrow J')I(\lambda)}{8\pi c n^2 \int \lambda I(\lambda) d(\lambda)} \quad (1)$$

where $I(\lambda)$ is the fluorescence intensity at wavelength λ, $A(J \rightarrow J')$ is the spontaneous emission probability for a transition from an excited manifold J to a lower manifold J', c and n are the velocity of light and refractive index of the crystal respectively. On the basis of the fluorescence spectrum and Eq. (1), the emission cross-sections of transitions from the $^1D_2$ manifold were calculated. During the calculation of emission cross-section of the $^1D_2 \rightarrow {}^3H_4$ transition, the contribution of emission from the $^3P_0 \rightarrow {}^3H_6$ transition around 606 nm was neglected because of the weak fluorescence intensity compared with that of the $^1D_2 \rightarrow {}^3H_4$ transition. Thus the emission cross-section at 606 nm was calculated to be 0.74×10^{-20} cm^2, which is comparable to 0.54×10^{-20} cm^2 of Pr^{3+}:$Sr_5(PO_4)_3F$ crystal that has been demonstrated to be a promising laser channel [3]. Moreover, the emission cross-section at 1038 nm was also estimated to be 1.93×10^{-20} cm^2, which is comparable to 2.3×10^{-20} cm^2 of Pr^{3+}:$NaBi(MO_4)_2$ crystal [15].

The values of the product of the emission cross-section σ_{em} and fluorescence lifetime τ_f for the $^1D_2 \rightarrow {}^3H_4$ transition, $\sigma_{em}\tau_f$, which is an important parameter in characterizing the laser threshold and efficiency [16], is 2.76×10^{-19} cm^2μs, which is comparable to those of oxide crystals, such as the estimated 1.15×10^{-19} cm^2μs of Pr^{3+}:La2(WO$_4$)3 crystal [17], 2.62×10^{-19} cm^2μs of Pr^{3+}:LaB_3O_6 of crystals which has been demonstrated the $^1D_2$ manifold to be a promising luminescent and upper laser level [12]. In addition, for the $^1D_2 \rightarrow {}^3F_3 + {}^3F_4$ transition at about 1038 nm which can be applied to underwater communications, the value of $\sigma_{em}\tau_f$ is 6.74×10^{-19} cm^2μs.

4. Conclusions

A Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal with dimensions of ϕ25×30 mm^3 has been successfully grown by the Czochralski method.. The absorption, fluorescence spectra and fluorescence lifetime of Pr^{3+} in Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal were investigated at room temperature. The absorption spectra is analyzed by the standard J–O theory and the modified J–O theory without the $^3H_4 \rightarrow {}^3P_2$ transition. Compared with the standard J–O theory, the reliability of the J-O parameters obtained by the modified J-O theory for Pr^{3+} ions has been improved. The crystal exhibited strong absorption band at 449 nm, which can be pumped with diode laser. The fluorescence lifetime and fluorescence quantum efficiency of the $^1D_2$ multiplets were estimated to be 34.9 μs and 27.5%, respectively. In comparison with the other Pr^{3+}-doped crystals, Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal has large emission cross-sections at 606 nm and 1038 nm, respectively. Except above, Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal has a large value of $\sigma_{em}\tau_f$ which is 2.76×10^{-19} cm^2 μs. To sum up, these results suggest that

Pr^{3+}:$Sr_3La_2(BO_3)_4$ crystal may be regarded as a potential candidate material for solid-state laser.

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