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Growth and spectroscopic characterization of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal

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Abstract

A crystal of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ with the dimension of $\phi 20 \times 30\,mm^3$ was grown by Czochralski method. The grown crystal was characterized by X-ray diffraction and DSC analysis. The DSC analysis showed that the crystal congruently melt at 1306.7°C. The absorption and emission spectra of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ were investigated. The absorption band at 806 nm has a FWHM of 13 nm. The absorption and emission cross-sections are $2.33 \times 10^{-20}\,cm^2$ at 806 nm and $1.58 \times 10^{-19}\,cm^2$ at 1062 nm, respectively. The luminescence lifetime τ_f is 75 μs at room temperature.

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Keywords: A1. Optical microscopy; A2. Growth from melt; B1. Borates; B2. Solid-state laser materials

1. Introduction

With the increasing interest in diode-pumped solid-state lasers, research on more efficient new materials for diode pumping becomes important. The double borates are a type of excellent laser gain media, for example, Nd^{3+}-doped $RAl_3(BO_3)_4$ (R = Gd or Y), and $RCa_4O(BO_3)_3$ (R = Y, Gd or La) are widely known laser medium materials [1–5]. The Cr^{3+}- or Ti^{3+}-doped $RX_3(BO_3)_4$ crystals ($R = Y^{3+}$, Gd^{3+} or the lanthanide; $X = Al^{3+}$, Sc^{3+}) can be regarded as the tunable laser gain medium [6–13]. Another type of double borate with formula $M_3R(BO_3)_3$ (M = Ba, Sr and R = La−Lu, Y, Sc) was recently reported as a new laser host materials [14–18]. The Stack family with formula $A_6MM'(BO_3)_6$ where A = Sr, Ba, Pb or Ln (Ln = lanthanide) and $M, M' = +2, +3$, or $+4$ metal cations [19–24] belongs to the trigonal system with $R\bar{3}$ space group [19]. Since the active ions such as Nd^{3+} or Yb^{3+} can substitute for Ln or +3 metal cations of Stack family crystals, we select $Sr_6GdSc(BO_3)_6$ crystal which is one member of the Stack family as our research aim. In this paper, we report the growth and spectral properties of Nd^{3+}-doped $Sr_6GdSc(BO_3)_6$ crystal.

2. Crystal growth

The raw materials of $Sr_6GdSc(BO_3)_6$ were prepared by means of solid-state reaction. The chemicals used were $SrCO_3$ and H_3BO_3 with 99.9% purity, and Nd_2O_3, Gd_2O_3 and Sc_2O_3 with 99.99% purity. The raw materials of Nd^{3+}-doped $Sr_6GdSc(BO_3)_6$ crystal were weighed according to the following chemical reaction equation:

$$\tfrac{x}{2}Nd_2O_3 + 6SrCO_3 + 6H_3BO_3 + \tfrac{1-x}{2}Gd_2O_3 + \tfrac{1}{2}Sc_2O_3 = Nd_xSr_6Gd_{(1-x)}Sc(BO_3)_6 + 9H_2O\uparrow + 6CO_2\uparrow.$$

The excess quality of 3 wt% H_3BO_3 was added to compensate the evaporation of H_3BO_3 during the growth. After grinding and extruding to form pieces, the samples were placed in a platinum crucible and held at 1100°C for 48 h to prepare the polycrystalline materials.

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Nd^{3+}-doped $Sr_6GdSc(BO_3)_6$ (8 at%) was grown by Czochralski method in a 2 kHz frequency furnace heating a platinum crucible in air. The charge was melt in platinum crucible with 50 mm diameter and 40 mm high. After repeating the seed and adjusting the heating power of furnace, Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal was grown at a pulling rate of 0.5 mm/h and a rotating rate of 10 rpm. The growing temperature was about 1300°C. Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystals with few cleavages were obtained. The maximum dimension was up to ϕ $20 \times 30\,mm^3$. Fig. 1 shows a polished piece and manufactured laser road.

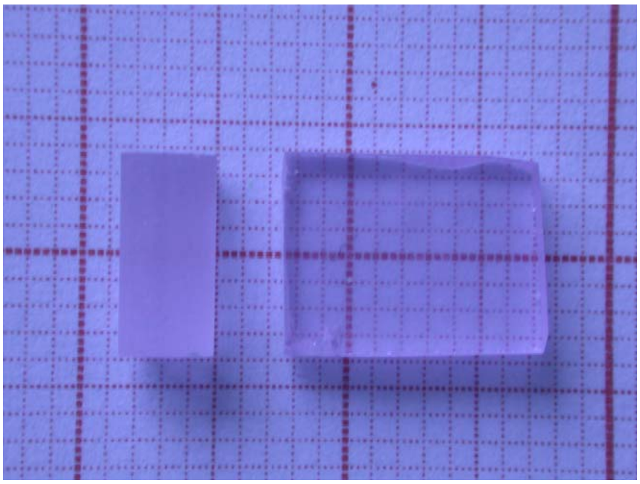

Fig. 1. Polished piece and laser road of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal.

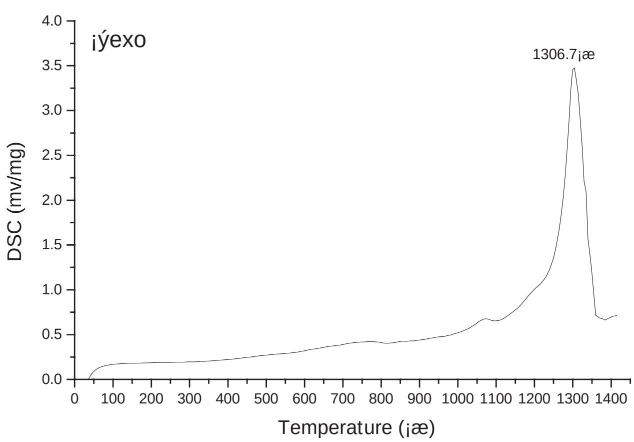

Fig. 2. The DSC curve of $Sr_6GdSc(BO_3)_6$ compound.

To confirm the melting point of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal, DSC measurement was performed up to 1400°C at a heating rate of $10°C\,min^{-1}$ in air using aNETZSCH-449C Thermal Analyzer. The result of DSC analysis showed that Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal congruently melt at 1306.7°C as shown in Fig. 2. The structure of $Sr_6GdSc(BO_3)_6$ crystal was determined by a Simens SMART CCD diffractometer with Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation at room temperature. The result shows that the crystal belongs to trigonal system with space group $R\bar{3}$ and $a = 12.415(2)$, $c = 9.274(2)$ Å, $z = 3$. Fig. 3 shows the X-ray powder diffraction pattern of $Sr_6GdSc(BO_3)_6$ crystal, which was obtained using a D-max-rA type diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.54056$ Å) at room temperature.

3. Spectroscopic characterization

A sample with dimension $9.7 \times 12.0 \times 2.2\,mm^3$ was cut from as-grown Nd^{3+}: $Sr_6GdSc(BO_3)_6$ and used to the spectral experiments (Fig. 4). The absorption spectrum was measured using the Perkin Elmer UV-VIS-NIR Spectrophotometer (Lambda-35). Photoluminescence spectrum and fluorescence lifetime were measured using an Edinburgh Instruments FLS920 LiseSpec PS spectrophotometer.

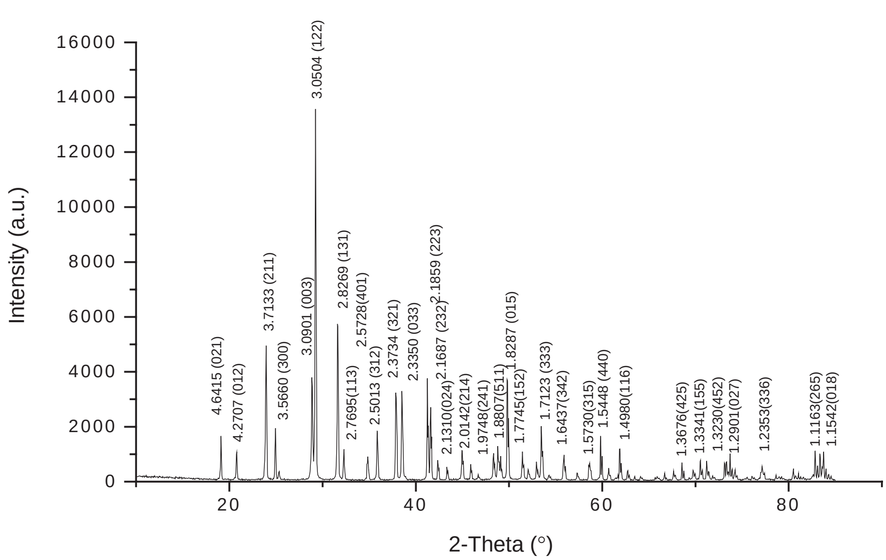

Fig. 3. X-ray powder diffraction pattern of $Sr_6GdSc(BO_3)_6$ crystal.

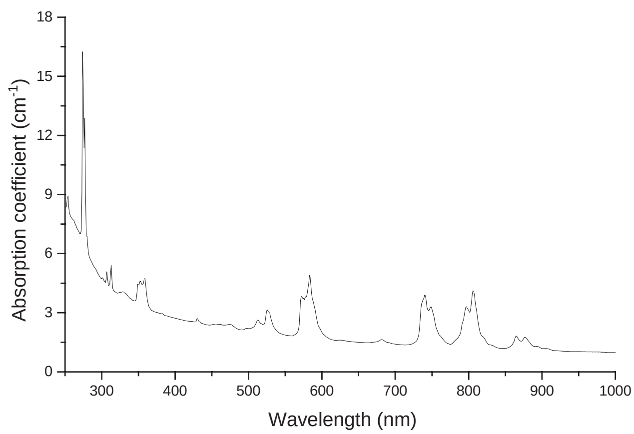

Fig. 4. Absorption spectrum of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal.

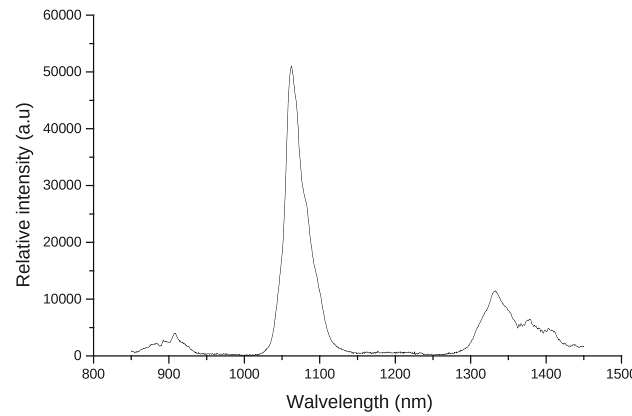

Fig. 5. Fluorescence spectrum of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal.

In the absorption spectrum the strong absorptions occur at near 275, 325, 359, 526, 583, 740, 806 and 865 nm. As well known, the rare earth atoms have the configuration $1s^22s^22p^63s^23p^63d^{10}4s^25s^25p^64f^n5d^16s^2$ ($n = 1-14$), the trivalent rare earth ions (RE^{3+}) in solids lose all 5d and 6s electrons. Since the optically active 4f electrons are shielded by the outer shell electrons, the 4f electrons of RE^{3+} ions in crystals are not strongly affected by neighboring ligands. In consequence, they produce only small energy splitting, and the gross features of the energy level diagram of RE^{3+} ions in different hosts are unchanged. Then, the assignments of RE^{3+} ion transition from the ground state to excited states can be determined by comparison with the energy levels of RE^{3+} ions in the LaF_3 crystals which was calculated by Carnall et al. [25]. Therefore, the absorption lines at 359, 526, 583, 740, 806 and 865 are due to $4f^3-4f^3$ transition of Nd^{3+} ions, the observed sharp absorption lines at 275 and 325 nm are due to $4f^7-4f^7$ transition of Gd^{3+} ion. The absorption band at 806 nm has a full-width at half-maximum (FWHM) of 13 nm, which closes to the laser output of AlGeAs diode-laser ($\lambda \approx 808$ nm). Since the emission wavelength of diode-laser is increased at 0.2–0.3 nm/°C with the operating temperature of laser device, the temperature stability of the output wavelength of diode-laser is needed to the crucially control. Therefore, such large line-width in Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal is very suitable for diode-laser pumping, since it is not crucial to temperature stability of the output wavelength of diode-laser. The absorption cross-section σ_a was determined using $\sigma_a = \alpha/N_c$, where α is absorption coefficient, N_c is the concentration of Nd^{3+} in Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal. which is $1.8 \times 10^{20}\,cm^{-3}$. The Nd^{3+} ion concentration in $Sr_6GdSc(BO_3)_6$ was determined by electron probe microanalysis method with an EPM-810Q instrument, where three samples cut from the top, middle and bottom of crystal were used to measured the Nd concentration. Then the Nd^{3+} ions concentration in Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal was calculated to be average 7.3 at%, i.e. $1.8 \times 10^{20}\,cm^{-3}$. The segregation coefficient η of Nd^{3+} ion in Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal is 0.91, which is defined as: $\eta = Nd^{3+}$ concentration in the crystal/Nd^{3+} concentration in the initial charge. Then, the absorption cross-section σ_a is $2.33 \times 10^{-20}\,cm^2$ at 806 nm.

Fig. 5 shows the photoluminescence spectrum of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal. The three emission bands at 850–945, 1020–1150 and 1290–1450 nm are due to the ${}^4F_{3/2} \to {}^4I_{9/2}$, ${}^4F_{3/2} \to {}^4I_{11/2}$ and ${}^4F_{3/2} \to {}^4I_{13/2}$ transitions, respectively. The fluorescence lifetime τ_f was measured to be 75 μs.

The emission cross-sections σ_e can be expressed as follows:

$$\sigma_e(\lambda) = \beta \frac{\lambda^2}{4\pi^2 \tau_f n^2 \Delta v}, \tag{1}$$

where λ is emission wavelength, i.e. lasing wavelength, τ_f is the fluorescence lifetime, Δv is the half-width frequency and n is the refractive index which is 1.73, β is the fluorescence branching ratios of the line which was calculated by integration of the fluorescence spectrum using

$$\beta = \frac{\int_a^b I(\lambda)\, d\lambda}{\int_0^\infty I(\lambda)\, d\lambda}. \tag{2}$$

Then, the fluorescence branching ratios β of radiative decay from ${}^4F_{3/2} \to {}^4I_j$ are as follows: β_1 (900 nm) = 0.0577, β_2 (1062 nm) = 0.6509, β_3 (1330 nm) = 0.2943. Thus, the emission cross-sections σ_e corresponding to ${}^4F_{3/2} \to {}^4I_{11/2}$ transition is $1.58 \times 10^{-19}\,cm^2$ at 1062 nm. Since the values branching ratios of β_1 (900 nm) and β_3 (1330 nm) = 0.2943 are smaller than the one of β_2 (1062 nm), and the values of Δv for the ${}^4F_{3/2} \to {}^4I_{9/2}$ and ${}^4F_{3/2} \to {}^4I_{13/2}$ transitions are larger than the one of ${}^4F_{3/2} \to {}^4I_{11/2}$ transition, the emission cross-sections at 990 and 1330 nm are more smaller than the one at 1062 in terms of Eq. (1). The spectroscopic properties of

Table 1
Comparison of spectral values of Nd^{3+}:$Sr_6GdSc(BO_3)_6$ and other Nd^{3+}-doped borate crystals

Crystals	Nd^{3+} concentration ($\times 10^{-20}$ cm^{-3})	Lifetime (τ_f) (μs) ($\times 10^{-20}$ cm^2)	σ_a ($\sim$at 810 nm)	FWHM (nm)	σ_e ($\sim$at 1060 nm) ($\times 10^{-19}$ cm^2)	$\tau_f \times \sigma_e$ ($\times 10^{-23}$ cm^{2}s)	Ref.
Nd^{3+}:$Sr_6GdSc(BO_3)$	1.8	75	2.33	13	1.58	1.2	This work
Nd^{3+}:$LaSc_3(BO_3)_4$	5.1	118	7.1	3	1.3	1.5	[13]
Nd^{3+}:$YAl_3(BO_3)_4$	1.1	56	/	/	1.0	0.6	[26]
Nd^{3+}:$GdAl_3(BO_3)_4$	2.2	54	4.3	8.7	3.4	3.3	[3]
Nd^{3+}:$Sr_3Y(BO_3)_4$	1.24	73	2.17	18	1.88	1.4	[15]
Nd^{3+}:$Ba_3Y(BO_3)_4$	1.05	70	1.56	15	1.82	1.3	[17]

Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal were compared with that of other Nd^{3+}-doped crystal, which is listed in Table 1.

4. Conclusion

A crystal of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ with dimension $\phi 20 \times 30\,mm^3$ was grown by Czochralski method. The DTA analysis showed that the crystal congruently melts at 1306.7°C. The absorption and emission spectra of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal were investigated. The absorption band at 806 nm has a FWHM of 13 nm, which is suitable for diode-laser pumping. The absorption cross-section is $2.33 \times 10^{-20}\,cm^2$ at 806 nm. The emission cross-section is $1.58 \times 10^{-19}\,cm^2$ at 1062 nm. The luminescence lifetime τ_f is 75 μs at room temperature. In conclusion, Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal has a broad absorption, large absorption and emission cross-sections. As well known, the large absorption cross-section is available to possibly absorb the energy of pumping source and to improve the light–light conversion efficiency. The large emission cross-section easily achieves the lasing oscillation and obtains the more output power under same pumping power. To sum up these spectroscopic characterizations of Nd^{3+}: $Sr_6GdSc(BO_3)_6$ crystal, it is suggested that it may be regard as a potential solid-state laser material for diode-laser pumped.

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