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Growth and spectroscopic properties of Nd^{3+}-doped $Sr_3Y_2(BO_3)_4$ crystal

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Abstract

A new crystal of Nd^{3+}:$Sr_3Y_2(BO_3)_4$ with a dimension of Φ $15\times30\,mm^3$ was grown by the Czochralski method. The grown crystal was characterized using X-ray diffraction. The absorption and emission spectra of Nd^{3+}:$Sr_3Y_2(BO_3)_4$ were investigated. The absorption transition at 807 nm has an FWHM of 16 nm. The absorption and emission cross sections are $6.32\times10^{-20}\,cm^2$ at 807 nm and $1.07\times10^{-19}\,cm^2$ at 1065 nm, respectively. The luminescence lifetime τ_f is 51.7 μs at room temperature.

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1. Introduction

With the rapid development of diode-pumped solid-state laser, research on more efficient laser materials has gained greater importance. Some borate crystals, such as Nd:$GdAl_3(BO_3)_4$, Nd:$YAl_3(BO_3)_3$ and Nd:$LaSc_3(BO_3)_4$, have demonstrated good spectral and lasing properties [1–3]. Other Borate crystals, such as $ReCa_4O(BO_3)_3$ (Re = Y, Gd, La) and $M_3Ln(BO_3)_4$ (M = Ba, Sr and Ln = Y, Sc, La–Lu) [4–6], have attracted researchers as new potential laser host materials. Recently, a new borate family with the formula $M_3Re_2(BO_3)_4$ (M = Ca, Sr, Ba; Re = Y, La, Gd) was reported [7–9]. The growth and spectral properties of Nd^{3+}-doped $Ca_3Re_2(BO_3)_4$ (Re = Y, Gd, La) were investigated [10]. In this paper, we report the growth and spectral properties of Nd^{3+}-doped $Sr_3Y_2(BO_3)_4$, which is a member of $M_3Re_2(BO_3)_4$ (M = Ca, Sr, Ba; Re = Y, La, Gd).

2. Crystal growth

The chemicals used were Y_2O_3, Nd_2O_3, $SrCO_3$ and B_2O_3 with 99.99% purity. The stoichiometric amounts of raw materials were weighed. The raw materials of the $Sr_3Y_2(BO_3)_4$ crystal were synthesized by the solid-state reaction method. The excess quantity of 3 wt% B_2O_3 was added to compensate for the evaporation of B_2O_3 during growth. After grinding and extruding to pieces, the samples were placed in a crucible and held at 1050°C for 36 h to prepare the polycrystalline materials.

5 at% Nd^{3+}-doped $Sr_3Y_2(BO_3)_4$ crystals were grown by the Czochralski method in a 2 KHz frequency furnace by heating in an iridium crucible in N_2 atmosphere. In the Czochralski method, the iridium crucible is generally used because of its high melting point of over 2000°C. The charge was melted in an iridium crucible with 65 mm diameter and 40 mm height. After repeating the seed and adjusting the heating power of the furnace, the Nd^{3+}:$Sr_3Y_2(BO_3)_4$ crystal was grown at a pulling rate of 1–2 mm/h and a rotating rate of 15–30 rpm. The initial growth temperature was about 1300°C. Nd^{3+}:$Sr_3Y_2(BO_3)_4$ with a dimension of Φ

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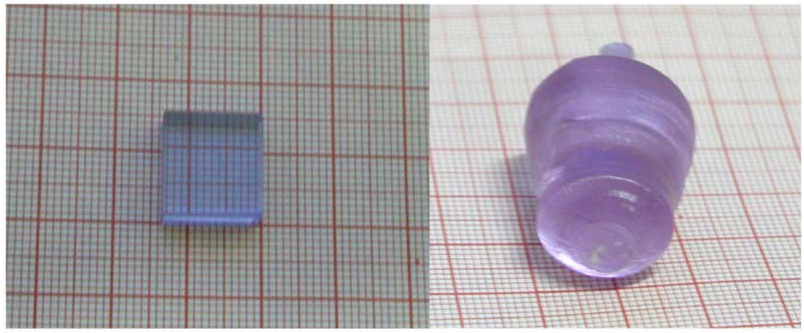

Fig. 1. The photograph of the grown Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal.

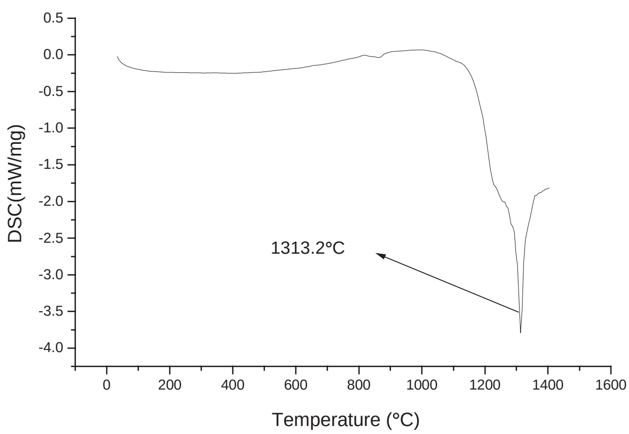

Fig. 2. DSC curve of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal.

$15 \times 30\,mm^3$ and free crack and inclusion was obtained, as shown in Fig 1. The surface of the as-grown crystal was opaque, because volatilized B_2O_3 corroded the surface of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal in the growing process. The result of DSC analysis shows that the melting point of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal is 1313.2°C, as shown in Fig. 2. The three samples cut from the top, middle and bottom of crystal were used to measure the Nd concentration. The content of Nd element in Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal was measured by the inductively coupled plasma and atomic emission spectrometer techniques to be an average 2.48 wt%. Since the active ions Nd^{3+} are substituted for Y^{3+} in Sr_3Y_2 $(BO_3)_4$ crystal, the Nd^{3+} ions concentration in Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ can be calculated as 5.85 at%. Thereby, the segregation coefficient of Nd^{3+} ion in Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal is 1.2, which coincides with that of Nd^{3+} ion in Nd^{3+}:Ca_3Y_2 $(BO_3)_4$ crystal [10].

The structure of Sr_3Y_2 $(BO_3)_4$ crystal was determined by a Siemens Smart CCD diffractometer with Mo$K\alpha$ radiation ($a = 0.71073\,\text{Å}$) at room temperature. The result shows that the compound Sr_3Y_2 $(BO_3)_4$ crystallized in the rhombic state with space group *Pnma* and $a = 7.4062\,\text{Å}$, $b = 16.0030\,\text{Å}$, $c = 8.7130\,\text{Å}$. The X-ray powder diffraction data were obtained using a D-max-ra type diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.54056\,\text{Å}$) at room temperature, which were indexed using the DICVOL program, as shown in Fig. 3.

3. Spectroscopic characterization

A sample of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal with dimension $2.5 \times 3 \times 3.5\,mm^3$ was cut from the as-grown Nd^{3+}:Sr_3Y_2 $(BO_3)_4$. The absorption spectrum was measured using the Perking–Elmer UV–VIS–NIR spectrophotometer (Lambda-35) at room temperature. Photoluminescence spectrum was measured at room temperature using an Edinburgh Instruments FLS920 LiseSpec PS spectrophotometer.

Fig. 4 shows the absorption spectrum of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal. The absorption band observed at 805–1050 nm is due to the transition of $4f^3-4f^3$ of Nd^{3+} ions. Strong absorption occurs near 395, 586, 749, 807, and 878 nm. In the absorption spectrum, the absorption band at 807 nm has FWHM of 16 nm, which is closer to the laser output of GeAlAs diode laser ($\lambda \approx 808$ nm). As is well known, the emission wavelength of the diode laser is increased at 0.2–0.3 nm/°C with the operating temperature of the laser device, the temperature stability of the output wavelength of the diode laser needs to be crucially controlled. Then such a large line-width in Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal is very suitable for diode-laser pumping, since it is not crucial to temperature stability of the output wavelength of the diode laser. The absorption cross section σ_a was determined using $\sigma_a = \alpha/N_c$, where α is the absorption coefficient, N_c is the concentration of Nd^{3+} ions in Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal which is $2.28 \times 10^{20}\,cm^{-3}$. Then, the absorption cross section σ_a is $6.32 \times 10^{-20}\,cm^2$ at 807 nm.

The luminescence spectrum of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal excited with 807 nm radiation is shown in Fig. 5. There are three emission bands corresponding to the $^4F_{3/2}-^4I_j$ transition, which were observed at 845–957, 1023–1140 and 1300–1427 nm. The luminescence lifetime of $^4F_{3/2}-^4I_j$ transition was measured to be 51.7 μs,

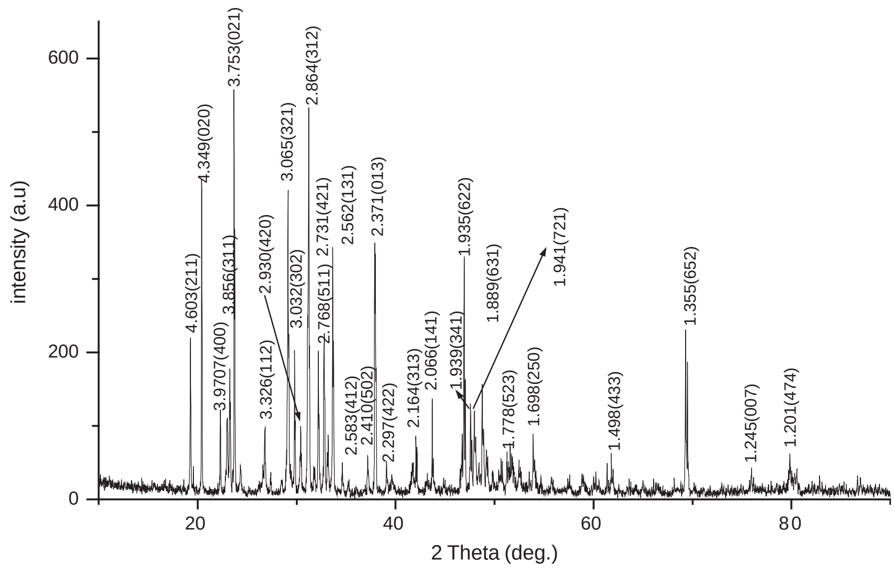

Fig. 3. X-ray powder diffraction pattern of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal.

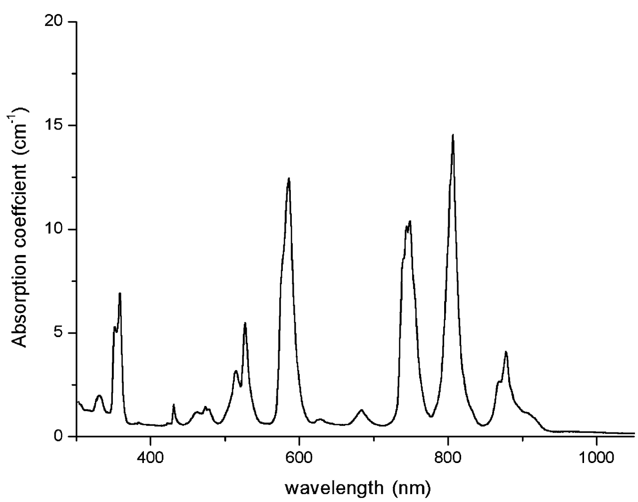

Fig. 4. Absorption spectrum of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal at room temperature.

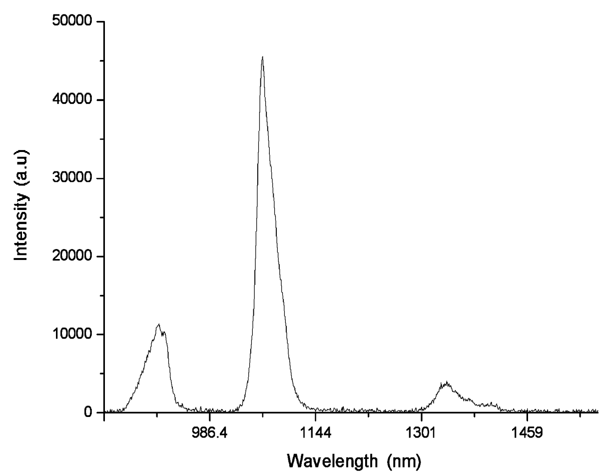

Fig. 5. Emission spectrum of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal at room temperature.

as shown in Fig. 6. The emission cross section σ_e at 1065 nm wavelength is determined by the following formula:

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

where β is the branding ratio, λ is the emission wavelength, τ_f is the fluorescence lifetime, Δv is the half-width frequency and n is the refractive index which is 1.74. Then, the emission cross section σ_e at 1065 nm is 2.06×10^{-19} cm^2. The spectroscopic properties of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal were compared with those of other neodymium-doped crystals, which are listed in Table 1.

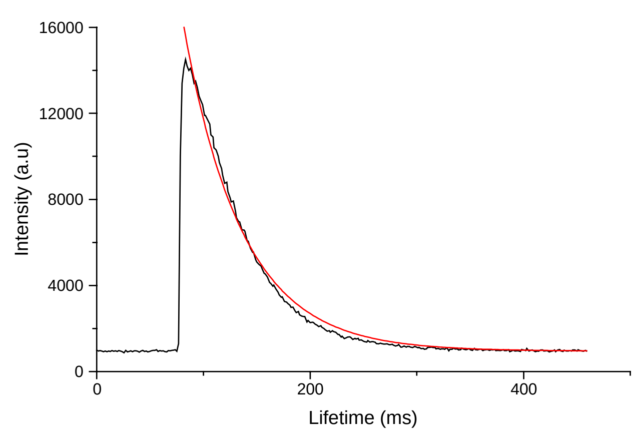

Fig. 6. Fluorescence decay curve of Nd^{3+}:Sr_3Y_2 $(BO_3)_4$ crystal at room temperature.

Table 1
Comparison of the spectroscopic properties of Nd^{3+}:$Sr_3Y_2(BO_3)_4$ crystal with other Nd^{3+}-doped crystals

Crystals	FWHM (~at 808 nm)	σ_a (10^{-20} cm^2) (~at 808 nm)	σ_{ae} (10^{-20} cm^2) (~at 1.06 μm)	τ_{em} (μs)	Ref.
5.85 at% Nd^{3+}:$Sr_3Y_2(BO_3)_4$	16	6.32	20.6	51.7	This work
2.5 at% α-Nd^{3+}:$Ba_3Y(BO_3)_3$	15	1.56	18.2	70	[11]
4.57 at% Nd^{3+}:$KY(WO_4)_2$	4	5.80	5.39	154	[12]
4.0 at% Nd^{3+}:$GdAl_3(BO_3)_4$	8.7	4.30	63.0	57.7	[13]
2.59 at% Nd^{3+}:$Sr_3Y(BO_3)_3$	18	2.17	18.8	73	[14]
3.3 at% Nd^{3+}:$LaVO_4$	20	3.00	6.13	137	[15]
$Sr_6NdSc(BO_3)_6$	18	1.46	1.18	48	[16]
Nd^{3+}:$LaCa_4O(BO_3)_3$	21	13.2	14.8	65.5	[17]
3.08 at% Nd^{3+}:$KLa(WO_4)_2$	12	7.6	80.0	157	[18]

4. Conclusion

A new crystal of Nd^{3+}:$Sr_3Y_2(BO_3)_4$ with a dimension of Φ 15×30 mm^2 and a few cleaves were grown by the Czochralski method. The absorption and emission spectrum of Nd^{3+}:$Sr_3Y_2(BO_3)_4$ have been investigated. The absorption cross section σ_a is 2.28×10^{-20} cm^2 at 807 nm. The absorption band at 807 nm has an FWHM of 16 nm, which is very suitable for diode-laser pumping. The luminescence lifetime is 51.7 μs at room temperature. The emission cross section σ_e is 2.06×10^{-19} cm^2 at 1065 nm wavelength. When compared with the other Nd^{3+}:$GdAl_3(BO_3)_4$ and Nd^{3+}:$KLa(WO_4)_2$ crystals, Nd^{3+}:$Sr_3Y_2(BO_3)_4$ crystal has a broad absorption band, large absorption and emission cross sections. As well known, the large absorption cross section in the laser materials is available to possibly absorb the energy of the pumping source, to improve the light–light conversion efficiency, to easily achieve lasing oscillation, and to obtain more output power under the same pumping power Therefore, these spectral characterizations of the Nd^{3+}:$Sr_3Y_2(BO_3)_4$ crystal suggest that it may be regarded as a potential solid-state laser material for diode laser pumping.

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References

[1] J-P. Meyn, T. Jensen, G. Guber, IEEE J. Quantum Electron. 30 (1994) 913.
[2] G.F. Wang, Z. Lin, Z. Hu, T.P.J. Han, H.G. Gallagher, J-P.R. Wells, J. Crystal Growth 233 (2001) 755.
[3] D. Jaque, J. Capmany, Z.D. Luo, G. Sole, J. Phys.: Condens. Matter 9 (1997) 9715.
[4] G. Aka, A. Kahn-Harari, D. Vivien, J.M. Benitez, F. Salin, J. Godand, Eur. J. Solid State Inorg. Chem. 33 (1996) 727.
[5] M. Iwai, T. Kobayashi, H. Furaya, Y. Mori, T. Sasaki, Jpn. J. Appl. Phys. 36 (1997) 53.
[6] T.N. Khamaganova, N.M. Kuperman, Zh.G. Bazarova, J. Solid State Chem 145 (1999) 33.
[7] O.A. Aliev, P.F. Pza-Zade, L.R. Shakhalieva, Sci. Papers Azerbaidzhan State Univ. Ser. Khim. 4 (1970) 18.
[8] B.F. Dzhurinski, I.V. Tananaev, O.A. Aliev, Izv. Akad. Nauk. SSSR Neorg. Mater 4 (1968) 1972.
[9] B.F. Dzhurinski, O.A. Aliev, I.V. Tananaev, Izv. Akad. Nauk. SSSR Neorg. Mater 6 (1970) 592.
[10] B.V. Mill, A.M. Tkachuk, E.L. Belokoneva, G.I. Ershova, D.I. Mironov, I.K. Razumova, J. Alloys Compd. 275–277 (1998) 275.
[11] S.K. Pan, Z.H. Hu, Z.B. Lin, G.F. Wang, J. Crystal Growth 247 (2003) 452.
[12] X.M. Han, G.F. Wang, J. Crystal Growth 247 (2003) 551.
[13] G.F. Wang, Z.B. Lin, Z.S. Hu, T.P.J. Han, H.G. Gallagher, J-P.R. Wells, J. Crystal Growth 233 (2003) 755.
[14] J.G. Pan, Z.S. Hu, Z.B. Lin, G.F. Wang, J. Crystal Growth 260 (2004) 456.
[15] L.Z. Zhang, Z.S. Hu, Z.B. Lin, G.F. Wang, J. Crystal Growth 260 (2004) 460.
[16] Z.B. Lin, Z.S. Hu, G.F. Wang, J. Crystal Growth 253 (2003) 265.
[17] Y. Lu, G.F. Wang, J. Crystal Growth 253 (2003) 270.
[18] X.M. Han, G.F. Wang, J. Crystal Growth 249 (2003) 167.