Optical study of Cr^{3+}-doped $LaSc_3(BO_3)_4$ crystal

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Abstract

This paper reports on the optical properties of Cr^{3+}-doped $LaSc_3(BO_3)_4$ (Cr^{3+}:LSB). Based on measurement of the absorption spectrum the crystal field strength Dq, the Racah parameters B and C were calculated. The photoluminescence spectrum of Cr^{3+}:LSB via $^4T_2 \rightarrow ^4A_2$ transition is a broadband emission from 740 to 1280 nm at room temperature. The measurements of absorption and photoluminescence spectra show that in Cr^{3+}:LSB the Cr^{3+} ions occupy weak crystal field sites.
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1. Introduction

There remains considerable research interest in the physics of tunable solid-state laser gain media. The focus of such interest is to expand the available pump and output wavelength of potential tunable laser, to develop more suitable pumping schemes especially those using flash-lamp and diode-laser as sources of pump radiation, and to enhance transition rates leading to greater laser efficiencies. The double borates $RX_3(BO_3)_4$ (R=Y, Gd, La, X= Al, Ga, Sc) are isostructural with the mineral huntite $CaMg_3(CO_3)_4$ [1], which can provide suitable sites for substitution by trivalent rare earth ion or trivalent transition metal ions in larger dopant concentration than in other crystals because of weaker luminescence quenching in this crystal structure [2–5]. Their excellent physical and chemical properties give $RX_3(BO_3)_4$ crystals significant potential as a gain media. The Cr^{3+}- or Ti^{3+}-doped $YAl_3(BO_3)_4$ (YAB), $GdAl_3(BO_3)_4$ (GAB), $YSc_3(BO_3)_4$ (YSB) and $GdSc_3(BO_3)_4$ (GSB) crystals as tunable laser materials have been reported several years ago [6–8]. The Nd^{3+}-doped $LaSc_3(BO_3)_4$, another member of $RX_3(BO_3)_4$ family, was reported as a high-efficient laser material for diode-pumped [9]. In fact, the $LaSc_3(BO_3)_4$ can also provide suitable sites for Cr^{3+} substituting Sc^{3+} ions to give rise to vibronic emission as well as the YAB, GAB, YSB, GSB. This paper reports preliminary optical study of Cr^{3+}-doped $LaSc_3(BO_3)_4$ (Cr^{3+}:LSB) crystal.

2. Experimental details

Cr^{3+}:LSB was grown by the Czochralski method. The stoichiometrically mixed raw materials of La_2O_3, Sc_2O_3; Cr_2O_3 and B_2O_3 were molten in a crucible in N_2 atmosphere. The Cr^{3+}:LSB crystal was grown at a pulling rate of 1 mm/h and a rotating rate of 10 rev./min. The Cr^{3+}:LSB crystal having diameter 15 mm and length 35 mm was obtained. The Cr^{3+} concentration was determined to be 3at.% by electron probe microanalysis. A sample of an arbitrary direction measuring $2.67 \times 3 \times 4$ mm³ was cut from the as-grown crystal and polished. Optical absorption spectrum was made at room temperature using a CARY-AVIV 14DS spectrophotometer capable of operating over the range 200~3000 nm. Photoluminescence at 300 and 20 K from the sample was excited using the multi-line visible output of an Ar^+ laser pumped rhodamine 6G dye laser tunable from 570 to 620 nm. Light emitted from the sample and detected at 90° to the excitation beam was focused onto the entrance slit of an 0.5 m grating monochromator and detected at the exit slit by a North Coast Scientific Ge detector.

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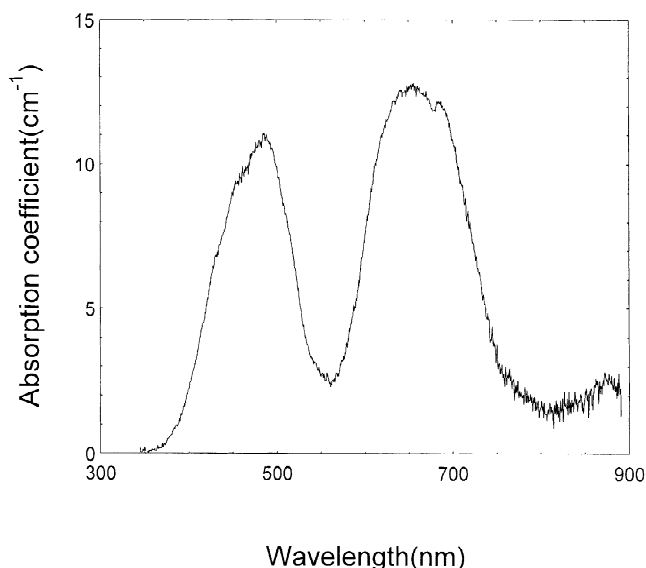
E-mail address: wgf@ms.fjirsm.ac.cn (G. Wang).

Fig. 1. Absorption spectrum of Cr^{3+}:LSB crystal at room temperature.

3. Results

The optical absorption spectrum of Cr^{3+}:LSB crystal measured at 300 K is shown in Fig. 1. The dominant features of absorption spectrum are two broad bands with peaks at 457 nm due to the $^4A_2 \rightarrow {}^4T_1$ transition and at 654 nm due to the $^4A_2 \rightarrow {}^4T_2$ transition, respectively. The R lines from the spin-forbidden $^4A_2 \rightarrow {}^2E$ transition in Cr^{3+}:LSB crystal were not observed. The dip near 678 nm in the $^4T_2$ band is characteristic of low crystal field Cr^{3+} hosts, which is also seen in $ScBO_3$ [10], $KZnF_3$ [11] and $SrAlF_5$ [12]. This feature of the absorption spectrum is interpreted in terms of an interaction between the sharp intra-t_2^3 levels (^2E, $^2T_1$ and $^2T_2$) and the vibrationally broadened $^4T_1(t_2^2e)$ quasicontinuum, resulting in Fano-type antiresonance [13,14].

The optical absorption spectrum of the Cr^{3+}:LSB crystal is interpreted assuming that Cr^{3+} substitutes into the approximately octahedral Sc^{3+} sites in the Cr^{3+}:LSB crystal. The energies of the electronic state E(n) of the Cr^{3+} ion, which are determined by the crystal field strength, Dq, and Racah parameters B and C, are represented on Tanabe–Sugano diagram, as shown in Fig. 2, which plots E(n)/B as a function of Dq/B for constant value of the ratio C/B-4.8 [15]. The absorption spectrum of Cr^{3+} ion in crystal are dominated by the strong spin-allowed transition $^4A_2 \rightarrow {}^4T_2, {}^4T_1$. The energy separations of the $^4T_2$ and $^4T_1$ states from the $^4A_2$ ground state are very sensitive to Dq, the strength of the crystal field. In consequence, this absorption spectrum of Cr^{3+}:LSB crystal is broad reflecting the modulation of levels by vibrations of neighboring ions. The peak energy of the $^4A_2 \rightarrow {}^4T_2$ band measures $10Dq$, and an approximately estimated value of Dq has been derived from the spectrum in Fig. 1. The energy at the peak of the $^4A_2 \rightarrow {}^4T_1$ band depends on both

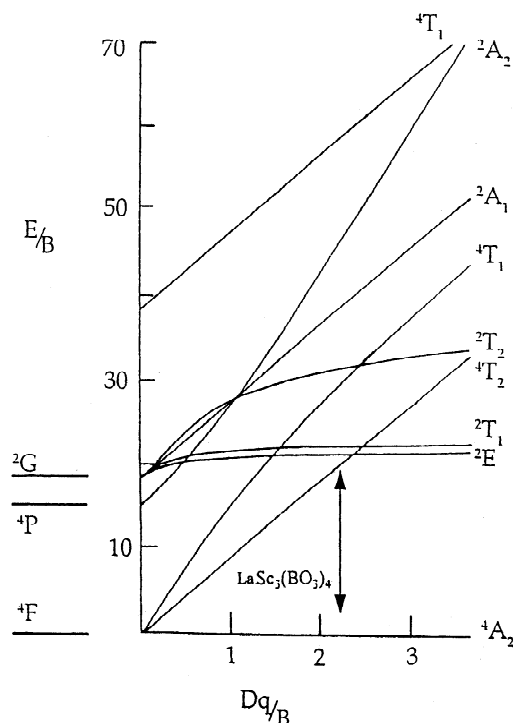Fig. 2. Tanabe–Sugano diagram.

Dq and B [16,17], if the δ is the difference in energy at the peaks of the two bands then B can be calculated as following

$$\frac{B}{Dq} = \frac{(\delta/Dq)^2 - 10(\delta/Dq)}{15(\delta/Dq - 8)} \tag{1}$$

Substituting the measured value of δ and Dq into Eq. (1) determines B. C was obtained from following [17]

$$E(^2E) \approx 3.05C + 7.90B - 18.0B^2/\delta \tag{2}$$

The band positions and half-widths quoted in Table 1 were used to calculate the value of Dq, B and C, which are collected in Table 2.

The photoluminescence spectrum of Cr^{3+}:LSB measured at 300 and 20 K is shown in Fig. 3. The dominant feature of photoluminescence is only a broad band extend-

Table 1
Comparison of peak wavelengths and half-widths of Cr^{3+} transition in LSB with other Cr^{3+}-doped borate materials

| Material	LSB[a]	YSB[b]	GSB[b]	YAB[b]	GAB[b]
$^4A_2 \rightarrow {}^2E$ peak (nm)	684	/	/	684	686
$^4A_2 \rightarrow {}^4T_2$ peak (nm)	654	650	645	595	590
FWHM (cm^{-1})	2910	2810	2830	2730	2530
$^4A_2 \rightarrow {}^4T_1$ peak (nm)	457	460	458	425	422
FWHM (cm^{-1})	4277	3380	3100	3580	3400
$^4T_2 \rightarrow {}^4A_2$ peak (nm)	963	875	860	750	760
FWHM (cm^{-1})	1817	2590	2750	2310	2240

[a] This work.
[b] Ref. [6].

Table 2
Comparison of ligand field parameters for Cr^{3+}:LSB with other Cr^{3+}-doped crystals

Material	Dq (cm^{-1})	B (cm^{-1})	Dq/B	C (cm^{-1})	C/B
LSB[a]	1529	675	2.27	3448	5.1
Al$_2$O$_3$[b]	1664	640	2.60	3300	5.2
BeAl$_2$O$_4$[c]	1709	675	2.53	3245	4.8
YAB[d]	1680	672	2.50	3225	4.8
GAB[e]	1695	673	2.52	3380	5.0
YSB[e]	1539	644	2.39	–	–
GSB[e]	1563	638	2.45	—	—

[a] This work.
[b] Ref. [18].
[c] Ref. [19].
[d] Ref. [20].
[e] Ref. [21].
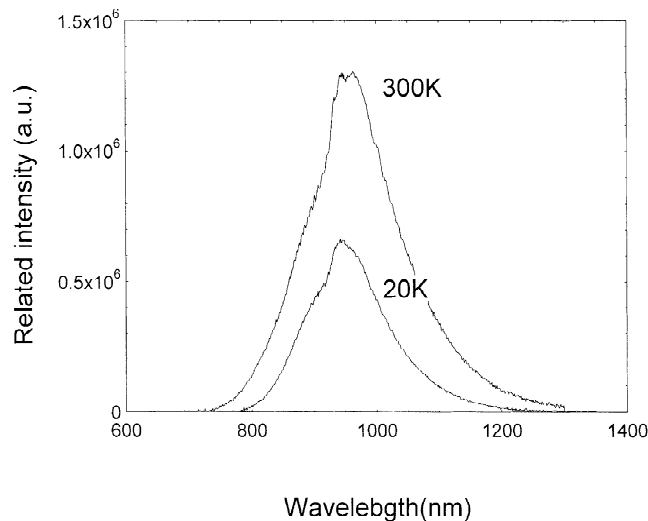
Fig. 3. Photoluminescence spectra of Cr^{3+}:LSB crystal at 300 and 20 K.

ing from 740 to 1280 nm with a peak at 963 nm and a full width at half maximum (FWHM) of 167 nm corresponding to the $^4T_2 \rightarrow {}^4A_2$ transition at 300 K. At 20 K the dominant feature of photoluminescence spectrum is still the broad
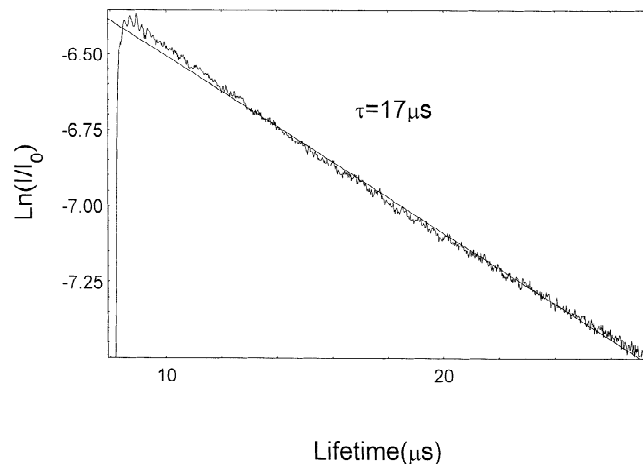
Fig. 4. Lifetime decay curve of Cr^{3+}:LSB crystal at 300 K.

band emission. It shows that the weak field site in the Cr^{3+}:LSB crystal gives rise to the Cr^{3+} luminescence in the $^4T_2 \rightarrow {}^4A_2$ transition alone.

The fluorescence decay of the $^4T_2 \rightarrow {}^4A_2$ transition of Cr^{3+}:LSB was measured at 300 K. The decay curve is almost exponential with identical lifetime of 17 μs, as shown in Fig. 4. In Cr^{3+}:LSB the higher Cr^{3+} concentration quenching causes the short lifetime. To reduce the Cr^{3+}-doped concentration would increase the lifetime in Cr^{3+}:LSB as well as the Cr^{3+}:YSB, Cr^{3+}:GSB and Cr^{3+}:LiCAF (see Table 3).

4. Discussion

The purpose of the present optical study of Cr^{3+}:LSB crystal is to assess its suitability as a potential tunable laser gain media. The absorption and photoluminescence spectra arise out of the weaker crystal field in Cr^{3+}:LSB. Chromium ions in the Cr^{3+}:LSB crystal are situated in a weak crystal field where the $^4T_2$ state is the lowest. In Cr^{3+}:LSB the $^4A_2 \rightarrow {}^4T_1, {}^4T_2$ broad absorption bands cover much of the visible region, which are ideal for flash-lamp pumping. Of course, the major interest in new Cr^{3+}-based lasers is in the potential for efficient pumping using visible diode lasers. For effective diode pumping the crucial

Table 3
Comparison of lifetime for Cr^{3+}:LSB with other Cr^{3+}-doped materials at 300 K

Material	Cr^{3+} concentration	Lifetime (μs)
LSB[a]	3 at.%	17
YSB[b]	0.2 at.%	109
YSB[b]	5 at.%	50
GSB[b]	0.2 at.%	132
GSB[b]	5 at.%	75
LiCAF[c]	0.31 at.%	171
LiSAF[d]	1.04 at.%	67

[a] This work.
[b] Ref. [22].
[c] Ref. [23].
[d] Ref. [24].

requirement is for strong absorption in the region 660–680 nm. On this point Cr^{3+}:LSB is entirely qualified, which has absorption coefficient at 670 nm exceeding Cr^{3+}:LiSAF by 45–50%. At room temperature the luminescence spectrum of Cr^{3+}:LSB has a broad emission of wide tunable range (740–1280 nm) with FWHM of 167 nm, of which peak output wavelength is shifted some 138 nm to longer wavelength than LiSAF. In consequence, the Cr^{3+}:LSB crystal may be of interest as a potential tunable laser material. The further works of Cr^{3+}:LSB are presently being addressed in the author's laboratory.

Acknowledgements

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